

THE DEVELOPMENT, DOCUMENTATION, AND APPLICATIONS OF THE  
INTEGRATED ENVIRONMENTAL, HEALTH, AND SAFETY INDEX (IEHS)

A Thesis

by

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Submitted to the Office of Graduate and Professional Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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August 2015

Major Subject: Safety Engineering

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## ABSTRACT

During the conceptual design phase of industrial processes, there is a need to make quick decisions on the screening and selection of alternatives. These decisions are typically based on techno-economic criteria and sometimes include environmental aspects. Safety considerations usually come as an afterthought. A designer charged with developing the conceptual process flowsheet for a new plant often cannot access the information needed for conventional safety analysis due to the lack of sufficiently detailed design data and time restraints. This is heightened in operations without extensive historical data such as processes that are small, produce specialty chemicals, or use novel processes. Given the significant gains that can accrue by including safety considerations during the conceptual design phases, there is a critical need to develop systematic approaches that aid the process designer in incorporating safety during the early stages of process design. This thesis turns a literature index into a process flowsheet development tool. The revised index is referred to as the Integrated Environmental, Health, and Safety index (IEHS). It accommodates the nature of early process synthesis and conceptual design work. It also accounts for categories not directly covered before such as maintainability, process control and overall process structure. The main focus of IEHS is to provide the designer with insights about the consequences of making design decisions and to provide a rational basis for the incorporation of safety issues on par with design methodologies and economic metrics. Through the use of IEHS, process designs failing to meet quantitative risk limits are eliminated from further consideration or revised to meet the desired limits early enough in the design work process. A case study is solved for the design of a dimethyl ether process to illustrate the applicability of IEHS in the early design phase.

## ACKNOWLEDGMENTS

I would like to thank Sara Badr, Stavros Papadokonstantakis and the process design group in ETH Zurich for giving me vital information on the previous indices, general shortcomings and roadblocks.

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## 1 INTRODUCTION

The early phases of flowsheet synthesis and conceptual process design are characterized by lack of time, an abundance of stress and numerous meaningful design decisions. There is a need to quickly assess different pathways toward an overall better design. A common approach is to conduct preliminary screening based on top-level economic feasibility. However, this may obstruct the effect of the decision in the economic translation process. Other process objectives such as operability, safety, and health, and environmental issues typically are not accounted for in the early design stages. Additionally, many hazards and design complications are first set in this phase. Therefore, there is a need to incorporate these issues in the early stages of process synthesis and design. A tool capable of predicting unacceptable designs likely to lead a high level of accidents, releases or shutdown time would address all of these concerns. This is in an effort to analyze the system holistically, eliminate unacceptable options and communicate early decisions to upper management.

The tool's approach is methodical accounting of all the different negative effects of a situation. To be used alongside more rigorous tools like process design tools and a technoeconomic study, the tool should primarily be based on defensible first principles and process phenomena. It is worth noting that if the procedure to use the index is lengthy, a designer is not likely to use it. The ease of access to the inputs and outputs of the assessment approach is crucial for the system to be useful. On the other hand, the designer needs to know exactly what goes into the procedure and must have the ability to change the data flow so that the procedure fits the conceptual-design needs. The output needs to have a clear path for a solution, or suggests the right questions to ask. This seems like a simple requirement, however even tools like a HazOp team or a safety expert may have difficulty meeting these goals. For a designer to complete the whole process of optimizing risk, the relevance to the process conditions need to identified so that corrective actions may be taken and feed back into the index. Additionally, choosing between alternatives and pathways in the design requires consistent metrics so that the



comparisons are meaningful and decisions can be quantified and justified. The whole range of values needs to be reliable and qualitatively associable so that the index can be set as a full constraint and not a boolean. This then requires both, a justification that is realistic and meaningful as well as an automated procedure. If these factors were to be realized, integration into a designer's workflow would be seamless. Developing the Environmental Health and Safety (EHS) index<sup>1</sup> into an index that addresses all these concerns and does this seamless integration with other process synthesis and conceptual design tools is the goal of this paper.

One of the most well-known tools for incorporating a safety assessment into the design phase is the Dow Fire and Explosion Index<sup>2</sup>. While it offers several advantages, it has some limitations because the variables are not continuous, the numbers have to be looked up in their own database and some of the data may not be available early enough in process synthesis. Additionally, many concerns and additions in this phase cannot be inputting into the formulation. This lack of resolution in the formulation results in a loss of information and a loss of some of the impacts of a design decision. Even though this index has been updated numerous times, has been automated<sup>3</sup> and even has been used for optimization<sup>4</sup> in terms of unsafe or safe, the fact remains that the main persuading power of the index is from expert opinion.

Another index is that is widely cited is Hazard identification and ranking system (HIRA)<sup>5</sup>. One of the features of this index divides and classifies process units based on their function. This is a necessary step for a design tool within the phase tasked with separating the process into different units. Many concerns were checked on a classification basis with an eye towards mirroring the first principle knowledge. These aspects will be taken almost directly from HIRA. The problem is the need for some numbers that will not be known in this early design phase like absolute distance away from other units. The fault in this index is that it did not go far enough with the first principle calculations, using stipulated penalty calculations right before an endpoint or qualitatively rich value could be obtained.

Throughout the literature there was a lack of quantifying environmental considerations, unit interactions and process control and other mitigation techniques. An environmental objective is seen as a subject that should be done by experts at the very end of the design when it is entirely too late or too costly to do any significant changes. Unit interactions or process structure hazards have been acknowledged before like in the Comprehensive Inherent Safety index (CISI)<sup>6</sup> but could not be accessed directly due to lack of failure data. In the Inherent safety index (ISI)<sup>7</sup>, these types of interactions were said to be unquantifiable and could only be assessed using case-based reasoning. Mitigating factors has often seen to be used as a credit system after the fact. An index that makes this a legitimate element is the Safety weight hazard index update of the HIRA index (SWeHI)<sup>8</sup> which takes into account human factors and mitigation solutions. The problem is, like HIRA, it is too detailed for this phase but can be adjusted to fit this need.

On a structural note, in the literature the question of control of the data flow comes into question. Dependencies and the manipulation of the data often have to go through statistical models or complicated aggregation schemes. If a designer wanted to use this index seriously, they would have to be confident in answering the question “Where did this number come from and what are its implications?” At a glance, they should be able to figure out what the value means and what specific aspect of the plant needs to be changed.

The EHS index proposed by Koller et al.<sup>1</sup> offers a different relationship with the data than other tools. The structure is modular with independent impacts called parameters like fire, acute toxicity etc. For a single parameter, it can accept multiple inputs across the spectrum of information quality with the default being SDS information. This allows for some malleability of the index to fit whatever useful information the end user has available. Additionally, this allows novel chemicals and reaction pathways to be included even if they did not exist when the index was created. The output is immediately digestible because the index ranges from zero to one with zero being a relatively benign situation and one being a dangerous situation. This comes

without loss of the underlying equations as it also shows exactly how the number was calculated with the parameters and the equations used. These equations are compiled through scaling of literature equations or regressions on empirical data. Both of these can be argued for or against by critics, developers or users and can be substituted for updated or corrected models without the need to invoke subjective opinions. For optimization, these equations are continuous and many are linearized versions of higher order equations. The proposed index uses the EHS index as a base because of these reasons. The two indices maintain these principles throughout but the IEHS index takes more situations taken into account, directly uses many models, and changes the general direction of the index toward process synthesis and conceptual design. The following section provides the details of these differences and the development of the proposed index.

## 2 OVERVIEW OF REVISED INDEX

The main EHS features can be found imbedded in IEHS as one set of parameter calculations called “method”. This is combined with other methods that make use of information that has emerged from this stage. The first method is *Chem.* which is the Initial Values from the EHS index done for modern databases and additional calculations. The Fate index and Technology factors are expanded for all the parameters and melded with other models into two new methods called *Secondary effects* and *Vessel*. Most of the equation level changes are made by going through the basic principles to get the relationships, often taking the calculations a step further towards these original equations. This simplifies the aggregation steps since one can assume that all the science will be found within the methods. For instance, the aggregation worries about chemicals in the EHS index and subsequent updates<sup>9, 10</sup> are alleviated by a new method, *Mix*, which calculates the interactions between the chemicals. Additionally, the parameters will be expanded from 11 to 13 by splitting up fire and explosion as well as runaway reaction probability and expected damage from a runaway reaction.

The EHS index requires updating for this phase because it was developed for the Input Output and reaction pathway phases of process development. The immediate impact of this is the amount of information that can be processed with the capability of a process simulator (e.g., ASPEN Plus) as well as the sheer number of units in a chemical plant. The end user of this index is working on a different problem and has to be able to control the flow of data for different objectives. Additionally, the abundance of stress and lack of time speckle this phase’s workflow much more heavily than the previous phase. These are the reasons behind the structural changes, automation efforts and the reworking of the base equations.

New models are introduced to bring in maintainability and operability into the early design phase. This is done through new methods called, *Vessel* and *Unit-Unit* that use failure rates and upset conditions respectively. Traditionally, these types of calculations have been omitted due to lack of information<sup>6</sup>, lack of confidence in the equations used<sup>11</sup> or a concentration on inherently safer. However, a tool’s omission of

the assessment of the defining quality of this phase, the individual units and their connections, should render it unusable. The procedure to build the individual equations of the previous models will be applied to these new methods so the numbers and formulations are comparable. However, the data collection is different as failure data, qualitative ranking systems and iterating over the rest of the index are quite different than gathering chemical hazard data. These calculations can only be done within a reasonable time with an automated system.

Along these lines, this index should be used as a tool for whatever questions the user has about a given PFD. Thus, it is not necessarily an inherent safety index since the information is parsed solely on its usefulness. However, a designer can use the index to find an inherently safer solution due to having enough resolution to source back problems at the plant level back to the chemicals. Another designer could also use the index to find the areas of higher risk and implement safeguards or optimize the plant to reduce one unit's impact. Additionally, inherently safer technologies can be added to the design through the Vessel method while other solutions can be inputted through changing the design directly. These solutions often fare better in the index due to being able to do the job more reliably than a risk reduction solution.

The merit of such design solutions is readily observed through the output of this index. The modular structure allows the end user to see exactly how much of an effect focusing on one area would have to the overall score. In this way, it sets up targets for each of the methods, the individual parameter, the chemicals and the units themselves. These are only theoretical targets in real life, but many equations are bounded between near benign to dangerous conditions. Therefore, many of these targets can be reached with optimization tools. Along with the use of filtering of the right information, and analyzing the entire plant as an interdependent system, this use of targeting is why the index can be called "Integrated."

### 3 APPROACH

With respect to ease of use and automation, the procedure of using the index should be quick, simple and easily incorporated into different workflows. There are three different parts to this system: the input, the program and the output.

#### 3.1 Input

The required inputs for the program to run are discussed in Table 1. For simplicity, csv, xls or xlsx documents are labeled as xls. The inputs are geared around multiple data inputs for a single scenario. One or more can be entered or left blank to default the analysis to the SDS or regulation requirements.

**Table 1. Description of the required inputs for the program to run.**

	Description	Sources	Format
Chemical Process Safety Sheet	Basic safety properties of all the chemicals that appear in the design.	SDS sheets, Literature, Online databases	.txt
Design information report	Process unit information	A simulator (e.g. Aspen Plus) / Rough hand calculations	.txt / .xls
Stream Table	A table of the properties of all the streams in the process.	A simulator (e.g. Aspen Plus) / Rough hand calculations	.xls
Chemical Reactivity Worksheet (CRW) <sup>12</sup> Report	A government program that simulates a solution to tell if there will be any evolved gases or side reactions	The report of the program with all the chemicals in one solution	.txt

The flexibility of these inputs using data readily available allows all designs in this stage to use this index. When a design is just an Input output structure, the index mostly reverts back to the scope of the original index. The changes are with the methods *Mix* assuming that any of the chemicals in the plant could come into contact with each other and *Vessel* using a plant-wide failure rate that can be changed for a specific process or industry with the availability of some semi-quantitative data or prior knowledge. On the other spectrum, the end of the design phase has vague information about siting and the unit specific economics that can be added to complement the analysis.

Along with the required sources, there is a number of additional information that the program can process. In terms of chemical properties there are two supplements to the process safety sheet, the simulator's chemical estimation report and the quantitative structure activity relationships (QSAR) values. The estimation report uses the power of the simulator to get correlations for many properties that are temperature dependent (e.g.  $C_p$ ) or otherwise (e.g. acentric factor). Without these the program has alternatives like generalized models, the ideal gas law or user inputted literature correlations. The QSAR calculations can predict properties of chemicals from quantum mechanical variables relayed to a statistical regression. This can be used to estimate toxicology, flash points and environmental variables for exotic or novel chemicals. The level of accuracy and the computing power required is dependent on the model used to predict these variables. For this application, a simple model is sufficient, so EPA's toxicity estimation software tool (TEST)<sup>13</sup> can be used which is free and includes the literature value if available.

In terms of how the program is run, there is also an input for user-weights and unit alterations. The user-weights allow a designer to customize the run and the aggregation to whatever is fit for the specific case study including using mass-weighted averages. The alterations worksheet is used to tell the program of any information not captured by the design information report. This includes process control, end of the pipe technologies, novel processes and mitigation measures. This is explained in detail in Section 4.

### 3.2 The program

The program was written in MatLab and runs with references and analysis types given in a separate configuration text file. This makes it easy to change the files or analysis types by changing the text file or writing a batch script. The program itself uses some nonlinear solving routines, but largely it uses basic algebra and recursion to compute the index. The program runs with minimal interaction, creating the templates for input files if they were omitted. Many values can be done by hand if need be and user specified weights can be used to customize the analysis. Run time for 36 unit plant with 12 chemicals was around 2 minutes with the number of chemicals being the biggest factor for speed.

### 3.3 The output

The output is an Excel spreadsheet with all the numbers and analysis. Every number is outputted with its justification or intermediate variables listed at the bottom. This could include what equation was used, the method added or the details of the aggregation step. The beginnings of a statistical analysis are done with a stream table and unit table ordering each using the index. From this, one can easily see the areas that are most at risk and exactly how with specifics on the parameter, method and chemicals in both output tables.



## 4 CALCULATIONS – DEVELOPMENT PROCEDURE

To develop all these equations and to satisfy the methodical portion of the goal, a rigorous procedure was used. One route is to use a literature variable or a predicated variable as a representative for a given parameter and method. Another route is to reproduce the detailed engineering calculations with a number of assumptions appropriate for the stage. This would result in some consequence or end point type variable that can be turned into an index using physical limits and accepted values. Other values that use more complicated models like *Vessel* or *Unit-Unit* ultimately use a combination of these two routes to transfer the derived variables into an index value. Below are two examples of this process. All the equations used are given in Table A.1.

### 4.1 Literature procedure

Early in the index, many variables are composed of literature values like regulations or recommended levels. These include things like flammability regions (LFL, UFL) or decomposition half-life. Other times, calculated variables are used either from key values in the base first principle proof, approximated literature values, nondimensional numbers governing the system. The procedure to develop the index calculation for this chosen variable is the same for both and is as follows:

1. Pick a phenomenon
2. Pick the parameter and method that the phenomenon best describes
3. Go through the literature and figure out which a key variable
4. Derive its relationship with end point values through a first principle equation or a correlation that tries to model some of the science.
5. Plot the distribution of this variable and its effects
6. Determine the scale (logarithmic, linear, etc.)
7. Pick a some indicative values (benign, dangerous, etc.) from known effects
8. Regress a line between the two values using:  $f(\text{benign point}) = 0$ ,  $f(\text{dangerous point}) = 1$

The first three steps are to find out the scope of the proposed index calculation in terms of what it is going to model (step 1), how will it be used in the overall structure of the index (step 2) and, most importantly, what will it use (step 3)? Going through how regulations are used in detailed calculations or what are the scientifically significant or useful equations on the subject. Here, “scientifically significant” means either a central first principle equation or a correlation that is physically relevant.

The rest of the steps involve the creation of the index. The equations that were studied in step 3, can be scaled for the given variable to get a relationship for step 4. Going through the literature and case studies to find the normal values for this index will produce the distribution in step 5. The scale of this distribution in step 6 can come from inspection or can be assumed from literature if you have, say, a correlation for a power law relationship. There are five indicative values that should be obtained for step 7: mostly harmless, benign, worrisome, dangerous and immediately dangerous to life. The final formula for the specific situation is found by regression on these points on the given scale to form a line. After this process, the developed function is inserted into the designated spot in the code and another calculation can be formulated.

#### 4.2 Model procedure

Many of the steps in the previous section can be circumvented with a rigorous model that predicts an end-point value directly. This end-point will often have some sort of qualitative scale or a physical scale that is immediately obvious to translate to an index. For example, take the end-point of “% permanently affected” from an exposure of a chemical. This has physical bounds at zero and one already built in. Additionally, one can grasp what the value means in terms of effects.

For the expected damage of a runaway reaction in the *Chem.* method, a direct model is used to get a value of percent of safety equipment destroyed. This was done by getting the TNT equivalent energy of all of that chemical in the unit. Assuming a loss of containment this energy was turned into overpressure at a certain distance. The distance used was 15 m which is the minimum recommended distance given by the CCPS. This overpressure was turned into percent of equipment damaged using a literature probit

calculation. To get an index value, the physical limit of 0% affected was used as a benign value and 50% as a dangerous value as shown below.

$$\text{Chem}_{\text{Exp.Damage}} = \frac{\% \text{ Affected}}{50}$$

## 5 DETAILS OF EVALUATING THE IEHS INDEX<sup>1</sup>

### 5.1 Structure and overview of the index

The structure of the index, shown in Figure 1, follows the path that the design makes from the input output structure in the previous phase to a completed flowsheet at the end of the phase. The index goes from an assessment of the chemicals and reactions, to a mixture of chemicals, to the material containing the process, to the different conditions in the unit, to a system of units connected together. Going from one step to another involves a set of assumptions about the design. When the chemicals are mixed together the assumption is that they do not interact with each other. The methods are supposed to correct for these assumptions.

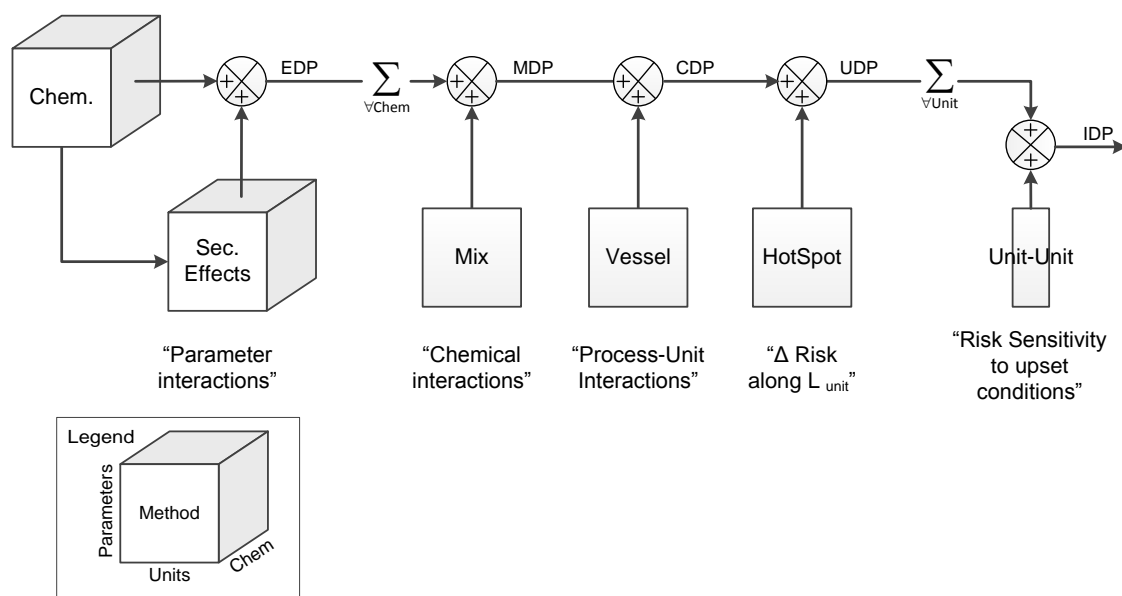
The problem is to get a real world assessment at every stage from a basis of the chemical used in the plant. Thermodynamics has a similar problem of getting approximations of properties that cannot be empirically tested for, like Gibbs free energy. One solution is to use residual properties to make use of something that is easy to calculate, like the ideal gas versions of the properties, and then add the effects of the residual properties to get a real value. In the same way, at each stage of the aggregation, the index will assume that the higher level effects are negligible by doing a simple sum of the values then try to adjust that number using the relevant method which assesses those higher level effects. These methods after the base calculation of *Chem.* have a range from -1 to 1 with -1 being helpful or dilution type effects and 1 being dangerous effects. The hope is that the values are centered on a value of zero or “no effect.”

The result of an aggregation is called a dangerous property as a nod to the original index. At the beginning there are three dimensions, the different chemicals, the

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<sup>1</sup> In this section, the calculation justifications are done in the context of a first assumption in the process flowsheet design phase. The assumptions used and the definition of the indicative index flags (benign and dangerous, etc.) are only applicable in this phase and with the context of these equations. Furthermore, these qualitative definitions are used for clarity. “Benign” values is really shorthand for “relatively benign or hazard undetectable by this calculation method”. This is the same for “dangerous” or any other qualitative value used from this point on. Furthermore this endeavor and most of the index was at least inspired by the original EHS index<sup>1</sup>.

unit that it is in and the parameter that it represents. At the final system-wide level, there should only be the different parameters to assess the hazards. The logical places in the design to collapse these other dimensions are shown in Figure 1, with the upper case sigma. The program default for this is to take the average, best case and worst case aggregation along that dimension. The parameters are done separately since the assumption that they affect one another is taken care of in the *Secondary effects* method. The end user can specify if they want custom weights or mass average weights in these collapsing steps. These are not defaults because the mass is already taken into account in the methods wherever science dictates. The result of this structure is shown in Figure 1.



**Figure 1. The overall structure of the index**

Quantities at a certain step in the design are designated as dangerous properties as a nod to the original index. In Figure 1 the steps of calculating the index is shown and laid out explicitly below.

1. Calculate *Chem.*, *Mix*, and *Vessel* parameters
2. Calculate *Sec. Effects* using information from *Chem.* and the input information
3. Add *Chem.* and *Sec. Effects* together to get Effective Dangerous Properties (EDP)
4. Aggregate the chemical dimension using user weights, average or worst case scenario
5. Add the *Mix* values to create the Mixed Dangerous properties (MDP)
6. Add the *Vessel* values to the MDP to create the Contained Dangerous properties (CDP)
7. Iterate steps 1-5 on the different conditions found in the unit and calculate *HotSpot*
8. Iterate steps 1-5 on the different upset conditions in the plant and calculate *Unit-Unit*
9. Add the *HotSpot* values to the CDP create the Unit Dangerous properties (UDP)
10. Aggregate the unit dimension using user weights, average or worst case scenario
11. Add the *Unit-Unit* values to create the Integrated Dangerous Properties (IDP)

As a basis, the chemical specific method, *Chem.* is assessed from the chemicals found within a unit and the process conditions. This is done on a chemical by chemical basis by going through their structure and their physical properties. The assumption used here is that the parameters themselves are not coupled with each other. With parameters like “Fire” and “Probability for a runaway reaction” it is safe to assume that one may lead to another. The situation becomes more dangerous when there is a chemical with multiple hazards that can trigger one another. Additionally, some of the information

about the chemicals may not be captured with just the chemical values like if a chemical was only appreciably toxic for one mode of intake. This is when the *Secondary effects* method is used to make the Effective Dangerous Properties (EDP). Design variables in this stage do not have that much sway over these methods so they are considered the chemical specific methods.

Next the chemical dimension is collapsed with the assumption that there are no interactions between the different chemicals. This is checked by the *Mix* method which goes through the interactions between all the chemicals in the solution. The equations that make up *Mix* are a combination of parsing the output of the chemical reactivity worksheet, some mixed versions of the equations in *Chem.*, and dedicated models for interaction effects. These are done as a solution where possible since binary interactions analyze a system that does not exist in the final product just like the chemical specific model. When this is added to the previous step it becomes the Mixed Dangerous Properties (MDP).

Another assumption that was used up until now was that the process units themselves will never break down or lose containment of the process. The *Vessel* method goes through a risk assessment for a loss of containment in each of the scenarios outlined by the parameters. A base failure rate from a lookup table for each ASPEN Plus simulation model is used by adjusting it with “unit conversion” type calculations. The units of the base failure rate are of “standard process conditions” and “without any alterations”. The model is first adjusted for the extremity of the process conditions, namely its temperature and pressure. This uses a given extreme condition for the process unit type and the failure rate if that unit reaches that condition. The design condition is assessed from a regression between the normal process condition and the extreme condition. The other adjustment is in the alterations on a unit, which can include everything from process control to end of the pipe technologies to a more rugged material of construction. Alterations are then anything about the design that is not included with the process unit type. The designer should have some thoughts about what units are easy to control or what additional gadgets are required for the design to run in

the next phase or already planned by the chemist. These are all vague ideas with an incredibly low amount of information or hard numbers. However, these adjustments should be able to swing risk assessments by orders of magnitude due to how closely they manage the risks of the plant.

This is accomplished with a semi-quantitative risk assessment on each of the proposed enhancements. First, the alteration is classified in how it helps the system in terms of changing the base failure rate, the failure rate for the extreme conditions, detection of a loss of containment or the mitigation of an event. It is classified into the specific parameters or dangerous conditions it protects against. The designer then evaluates the system using a ranking scheme and a rubric in the categories of strength, maintainability, and reliability. This introduces a wealth of possibilities for the types of systems that can be included. An inherently safer solution would have the benefit of high scores for maintainability and reliability but it still has to get high marks in strength, or in other words, do its job. Alternatively, if the problem can be easily solved with another material of construction or a thicker hull, the system would be able to see this with the same formulation. This area highlights how every method can be approached using an inherently safer approach or through a system level risk reduction point of view.

Once the process units are created, this *Vessel* method is added to the dangerous properties which create the Contained Dangerous Properties (CDP). Up until now, one condition was used to assess all the methods. For a reactor, a litany of properties is changing and some chemicals may even be emerging from the solution. These dynamics need to be captured by the system to accurately judge a unit over whole length of the unit. This is done in the method, *HotSpot* that redoes the index (up until the CDP) for the different conditions found in a unit. For all the conditions that can change, the index is redone on the base unit with that condition changed to the final value. The base unit is either an average value of the conditions or the output condition where appropriate (e.g. a CSTR). In the future, more conditions could be tracked and more intermediate points could be examined. The final value of *HotSpot* is equal to the difference between the average index value of all the conditions and the index value of the base condition used.



This is the error that would have happened if you just took the base condition as a representative for the entire unit. This is done for all the parameters and then added to the CDP to become the final unit-dependent value, named Unit Dangerous Properties (UDP).

The units are collapsed with the assumption that the units are not affected by each other. This is tested in the method *Unit-Unit* where the upset conditions are calculated. There are two parts of this problem: abnormal event mitigation and process control. The model generates different upsets using HAZOP methodology and then assesses how well the downstream units handle the upset. For the abnormal event mitigation, different upsets are created using guide words like “more” or “less” on different process conditions like pressure and temperature. On the process control side, these scenarios are tested in the model of the plant for risk, the index up to this point, and evaluated for “overshoot” from the model in the normal state. The qualitative definition of Unit-Unit is a measure of the robustness of the system to an upset for that stream. Once this is added to the combined version of UDP, the dangerous property is said to be representative of a system wide approach to the plant and is said to be an Integrated Dangerous Properties (IDP).

## 5.2 Chemical method (*Chem.*)

### 5.2.1 Overview

Initially, a designer would try to gather basic information about the chemicals and known hazards using available databases and the SDS information. This method is from the perspective of a first responder trying to decide what preventative measures should be used for an accident. The first thing that a first responder would look for is the SDS for the chemicals in a plant. The calculations have been updated for the new Global harmonized system, adopting their data as input and some of their characterization into the program. Throughout the calculations this value will be the last resort if there is no better information linking the data to the basic process conditions. Many other databases are used with the NOAA developed Chemical reactivity worksheet (CRW) program<sup>12</sup>

being adopted as a requirement. This program was made for first responders so it aggregates many different sources to display potential hazards, identifying numbers and some physical properties.

CRW has a large and rather definitive classification system for chemicals based on their functional group and potential danger. This is valuable information that will be used to figure out the best way to assess a hazard as well as a last resort assessment. A group designation of “Halogenating agents” would tip off the program to look for reactive hazards and potential halogen gases while an “Azide group” may be enough information to conclude explosive hazards.

This leads to a closer look at the molecular structure of the chemicals to predict hazards. For this, quantitative structure activity relationship or QSAR<sup>II</sup> can be used. This is a statistical model that combines many different descriptor variables to calculate various physical properties. The regression is done by calculating the properties with laboratory experiments and then finding the best statistical fit with the descriptors that they calculate. These descriptors are called molecular descriptors and are quantum mechanical relationships with the 3-d molecular structure of the chemical in question. These could be as simple as the number of nitrogen atoms or require substantial computing power to calculate. Basic quantities can be derived from the existence of functional groups, the molecular formula or the 3-D structure as shown through the Simplified Molecular-Input Line-Entry System or SMILES.

The accuracy depends on the rigorosity of the model used to calculate the descriptors and the quality of the original equation. Many different programs can output the descriptors for a molecule like Toxicity Estimation Software Tool (TEST)<sup>13</sup>, CheS-Mapper<sup>14</sup>, Molgen<sup>15</sup> or Chemical development kit (CDK)<sup>16</sup> with various levels of computational rigor. The statistical regressions are found in various academic papers and will be referenced as they are used in the index development. Many of the basic values

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<sup>II</sup> QSPR is a Quantitative structure property relationship whose only difference is that the final result is a chemical property instead of a biological or physiological like a QSAR. This distinction will be dropped from here on out as QSAR will be used to refer to both.

are outputted automatically as a sanity check, like boiling point. The level of rigor required for this index matches the TEST software's algorithms. It also automatically queries the EcoTox<sup>17</sup> database of reported values if available and gives a rather lengthy list of descriptors for literature QSAR products. Along with the fact that it is free and easy to use, TEST has most of the properties that are most important for this application.

### 5.2.2 Mobility

Mobility is the ability of the chemical to affect the party involved after loss of containment. The first thing to assess is the state that the chemical would be in after loss of containment. A simplified dispersion modeling is then done by scaling the effects from the chemical itself. The main input parameters involved in many dispersion models and mass transfer models are molecular weight and density. According to the physical state of the release, these variables will be transferred to indices as shown below.

For liquids, the concern is if it is held above its boiling point, it could flash with a loss of containment. The fraction that is flashed ( $f_v$ ) is used as the descriptor value<sup>18</sup>.

$$f_v = \frac{C_p * (T - T_b)}{\Delta H_{\text{vap}}} \quad \text{Eq. 1}$$

$$\text{Chem}_{\text{Mobility}} = 0.4 * (1 + f_v) \quad \text{Eq. 2}$$

All the values for mobility will be given ranges depending on the physical state of the chemical.<sup>III</sup> Here the chemical is still in a liquid state but is allowed to have an upper limit of one because of the added heat due to the latent heat of vaporization that could cause additional problems.

Otherwise the mobility for a liquid will be seen as a function of the volatility and the viscosity of the liquid. For volatility, the descriptor of choice is the equilibrium ratio or a K-value as shown below<sup>19</sup>.

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<sup>III</sup> If not otherwise stated, the output range of all the initial value calculations is from 0 to 1 no matter the range of the inputs. After the value from the equation is calculated the range is applied and if it is outside the range than the closest limit will be the index value.

$$K_i = \frac{\gamma_i P_i^{\text{sat}}}{P} \quad \text{Eq. 3}$$

This is measuring how much the chemical wants to be in the vapor phase and is defined as the mole fraction in the vapor divided by the mole fraction in the liquid. To calculate it, a modified Raoult's law will be used with the saturation pressure predicted from the Aspen regression as shown below with the index formulation.

$$\text{Chem}_{\text{mobility}} = \min \left( 0.6, 0.2 + \left( \frac{0.4 K_i}{50} \right) * \frac{1 \text{ cps}}{\mu} \right) \quad \text{Eq. 4}$$

Viscosity is taken in centipoise (cps) which is already weighted against water at 20° C so its inverse relationship with mobility is given without a multiplier. The nominal value for the K-value is for Ethane at atmospheric pressure and 60°C which is the benchmark which is set for a 0.6 dangerous level<sup>20</sup>. This is a non-flashing liquid so the range is taken from 0.2 to 0.6.

For a gas release, the major components are going to be from diffusivity and dispersion modeling. The descriptor values used are molar weight (*MW*), and density ( $\rho$ ), using a benign value of water and air respectfully. One factor is from the average velocity of rigid spheres found within diffusivity models like Chapman-Enskog. This adds a factor of the square root of molar weight. These models also use the mean free path calculation that use concentration in the form of the inverse of density<sup>21</sup>. From dispersion modeling, buoyancy is one of most used quick sanity and plausibility checks that should be done before any prediction. In terms of risk to the populace or the workers, denser gasses allow toxins to concentrate near the surface of the earth while lighter gases go into the atmosphere away from affected populations. Assuming an instantaneous release in the Bitter-McQuaid model this factor would then use an inverse square root relationship with the index as shown in the factor of one half in the exponent in the following equation.

$$\text{Chem}_{\text{Mobility}} = 0.5 + \sqrt{\frac{18 \text{ gm/mol}}{MW}} * \frac{\rho_{\text{air}}}{\rho} * \left| \frac{g * (\rho - \rho_{\text{air}})}{\rho_{\text{air}}} \right|^{\text{sign}(\rho - \rho_{\text{air}})/2} \quad \text{Eq. 5}$$

This has the highest lower bound for mobility (0.5) because gas releases are inherently dangerous and is trying to assess the worst case of a dense cloud release. Here

$g$  is the acceleration due to gravity and the “18 gm/mole” is from the molar weight of water. If the chemical is lighter than air (negative relative buoyancy), then the mobility value is given a value indirectly proportional to the relative buoyancy of the chemical. The heavier the chemical is, the situation would more likely to be dangerous, which requires a direct relationship the index value. The sign function returns the sign of the difference between the densities. Future work can include including the spherical radius of the chemicals from the molecular descriptors in the QSAR procedure.

Solids get a mobility of zero unless it is a dust which would depend on its size of the particles which is an area of future research.

### 5.2.3 Fire

For the potential for fire, the best value to use is the flash point temperature. This is the lowest temperature that has enough energy to cause a fire. This does not mean that a fire is imminent at this temperature due to the necessity of the other two parts of the fire triangle as well as the fact that it is a mass transfer problem to vaporize enough liquid to sustain a fire. There is a fire point that is also used which is the lowest temperature that a sustained fire can be seen. However, this parameter is for the chemicals' flammability which should not have mass transfer of the solution. The volatility is already in the mobility parameter so there would be double counting if it were used here. Using the process temperature, the flash point is turned into an index value through the following formula from the original index<sup>1</sup>.

$$\text{Chem}_{\text{Fire}} = 1 - \frac{(T_{\text{Flash}} - T)}{200^{\circ}\text{C}} \quad \text{Eq. 6}$$

A nominal value of 200 °C for the difference between the flash and process temperatures is used away from the flash point for a benign value as per the previous index. While being at or above the flash point will be seen as a dangerous fire hazard and will be assigned a value of one.

For new chemicals, the flash temperature can be predicted using ASPEN. The major energies at play in this process are the latent heat of vaporization,  $\Delta H_{\text{vap}}$ , and the

combustion energy,  $\Delta H_{\text{comb}}$ . This can be correlated with a nondimensional form of the flash point. The value that is used is the boiling point which is similar to the flash point and is readily available, easy to predict with a QSAR and a simple experiment to set up. The following correlation is from Valenzuela et al.<sup>22</sup>

$$\frac{T_{\text{Flash}}}{T_{\text{Boil}}} = 0.726 - 7.15 \times 10^{-5} * \left( \frac{\Delta H_{\text{comb}}}{\Delta H_{\text{vap}}} \right) \quad \text{Eq. 7}$$

The next most reliable parameter is the lower flammability limit (LFL) which addresses the issue of amount of fuel through composition in air. This along with the flash point is usually reported on the SDS. If it is not reported than this can be estimated using the stoichiometry of the combustion reaction and an empirical formula as shown below<sup>18</sup>.

$$\begin{aligned} C_{\text{st}} &= \frac{100}{1 + z/0.21} \\ LFL &= 0.55C_{\text{st}} \\ UFL &= 3.50C_{\text{st}} \end{aligned} \quad \text{Eq. 8}$$

The stoichiometric amount of fuel ( $C_{\text{st}}$ ) is calculated using the amount of oxygen molecules stoichiometrically required for the combustion reaction ( $z$ ).

The next step would be to adjust the LFL for a given temperature. LFL is a function of equilibrium conditions and then vary with temperature. Pressure has a small effect on LFL so its effect will be assumed to be constant. This has to be calculated experimentally but may correlations exist to relate it to other important flammability characteristics, like the combustion energy. The following correlation will be used for this index<sup>18</sup>.

$$LFL_T = LFL_{25} - \frac{0.75 \% \text{ vol } \frac{\text{kcal}}{\text{mol} \cdot ^\circ\text{C}}}{\Delta H_{\text{comb}}} (T - 25^\circ\text{C}) \quad \text{Eq. 9}$$

The LFL at 25 °C that was calculated or obtained earlier is  $LFL_{25}$ , while the temperature scaled version is  $LFL_T$ . This can be turned into an index following the rule of thumb that an LFL more than 15 wt.% is near harmless.

$$\text{Chem}_{\text{Fire}} = 1 - \frac{LFL_T}{15 \text{ wt}\%} \quad \text{Eq. 10}$$

The other side of the fire triangle is the amount of oxygen. The lowest concentration of oxygen that can cause a fire is called the lowest oxygen concentration or the LOC (also called the minimum oxygen concentration, MOC). This can be estimated from the stoichiometry again as shown below or it could be listed on the SDS or on an online database<sup>18</sup>.

$$LOC = z * LFL \quad \text{Eq. 11}$$

If this formula is used without a literature value for the LFL, then the reliability of this formula goes down since this is using the same approximation twice. This is transferred to an index as shown below.

$$\text{Chem}_{\text{Fire}} = 1 - \frac{LOC - 5 \text{ wt}\%}{25 \text{ wt}\%} \quad \text{Eq. 12}$$

Anything around 25 wt.% requires more oxygen than in air which probably means it is not that flammable. Below 5 wt.% the prediction becomes unreliable so LOCs in this range would predict the same level of dangerous flammability.

#### 5.2.4 Acute toxicity

For releases over a small time scale, inhalation is the major route of entry. The worry is that the exposure would overwhelm a human's defense system. This is best expressed by the threshold limit value for the ceiling for concentration, TLV-C, which is defined as the concentration that should never be exceeded no matter the time frame of exposure. Most likely the SDS will have a TLV-STEL value or the short term exposure limit of the chemical. This is for the maximum concentration allowable over a short time frame of either 15 or 20 minutes. With the level of scrutiny of this index, either value will give the same results. There are many different sources for this information, but ACGIH's values are usually the best with the ability to be easily updated and with direct knowledge of the experiments themselves.

Other values that can be helpful are the IDLH or the immediately dangerous to life and health which is compiled by NIOSH. This value was developed for respirators and represents the concentration that will cause irreparable harm over the long or short term from a single exposure. This includes irritants and asphyxiants that can prevent escape from dangerous environments so the value must be used carefully. All these values are on the same scale with the same implications and mitigations so the index formulation is the same. The difference is the priority of the values which should go, TLV-C, TLV-STEL then IDLH.

$$\text{Chem}_{\text{AcuteTox}} = 1 - 0.25 * \log_{10}(\text{IDLH} / 10\text{ppm}) \quad \text{Eq. 13}$$

The nominal value would be 10 ppm which would garner an index of 1 while a value at 10 % could be more deadly as a physical asphyxiant than from its toxicity so it gets a value of 0.

If these values cannot be found and the only information is from a toxicology study in a research paper or in the SDS, the concentration where half the specimen were killed through inhalation, or the  $\text{LD}_{50,\text{Inhal}}$ , can be used. Toxicology studies are often done with a variety of concentrations on a certain subject given a certain time that the subject is exposed to the substance. The time of the exposure distinguishes between acute effects and chronic effects as scaled to the lifecycle of the subject. The researcher determines the variability and confidence when extrapolating to humans diminishing the authority of the results. Different response variables could be used like the effective dose for positive attributes ( $\text{ED}_{50}$ ) or other specialty situations like the value at which 50% of the population has its growth inhibited,  $\text{IGC}_{50}$ . This also comes in different percent values to capture more of the dynamics of the dose response curve. The approximation with the organism and the sometimes dubious reliability of this value leave it at the bottom of potential values to use.

$$\text{Chem}_{\text{AcuteTox}} = 1 - 0.5 * \log_{10}\left(\frac{\text{LC}_{50,\text{Inhal}}}{100\text{ppm}}\right) \quad \text{Eq. 14}$$



This comes from classical toxicity classes that are used often to extrapolate these values to human exposure in a proper risk assessment<sup>23</sup>. The two values approximated are a dangerous value of below 100 ppm and a nontoxic value at 10,000 ppm.

#### 5.2.5 Probability of a runaway reaction

A runaway reaction starts with a reaction unexpectedly proceeding faster than usual. This is the initiating event that may cause other side reactions and the decomposition of the chemical leading to more instability. Eventually this results in a change in the pressure or temperature away from the design conditions. Deviations cause more decomposition and unwanted reactions in a positive feedback loop causing more instability and a medley of other harmful effects including explosion, fire and corrosion. The probability of the initiation event is a function of the entire mixture and is best assessed in the mixing factors. The probability of the chemical decomposing is a function of the chemical's stability and is assessed here.

The first check you would make would be the adiabatic temperature rise from the given reaction or from the energy of decomposition. Side reactions can be used if they are known. If the cooling shuts off or some sudden upset happens, the rise in temperature from the reactions can cause other reactions and more instability. If the temperature rise is small the mixture it would be hard for a chain reaction to happen unless the mixture was particularly sensitive to pressure which is often not the case.

The next value that can be used is the auto ignition energy or the AIT. This is the temperature that the chemical can combust using its own kinetic energy as the ignition temperature. Ignition energy is a function of the stability of the molecule or the activation energy of the combustion reaction. The difference between this and the design temperature is transferred to an index like in the previous index as follows<sup>1</sup>.

$$\text{Chem}_{\text{ProbRun}} = 1 - \frac{(AIT - T)}{200^{\circ}\text{C}} \quad \text{Eq. 15}$$

Just like with the flash point calculation this was made as a linear regression between the conditions of 200°C away from the AIT is used as a benign value and at the AIT is used as a dangerous condition.

Additionally, common functional groups that cause stress on the molecule or are inherently unstable, like enol or hemiacetals, are deemed to be dangerous depending on their number and percent of the entire molecule. This is done using the classification by the CRW program. The percent of atoms in such a dangerous functional group is a major factor since the rest of the molecule could stabilize it with its 3-D structure. In the future a specific QSAR relationship will be used to determine the stability of the molecule expanding on this thinking.

#### 5.2.6 Expected damage

The damage that such a reaction could produce is a much more concrete parameter than the probability. Here the enthalpy of decomposition can be used to estimate the effect of the chemical in question. If this energy is not known, combustion energy and Gibbs free energy can be substituted in that order of preference. These would be the extensive versions derived from Hess's law which would incorporate the amount of inventory in the reactor. How much of this energy will be given transferred to an explosion is given by the efficiency,  $\eta$  and will be given a nominal value of 5% accounting for less than ideal mixing of the gas and the inevitable loss of work due to conversion between thermal to mechanical energy. To assess the consequences of such an explosion, this energy would then be compared with the equivalent mass of TNT using a slightly changed TNT equivalency method as shown below<sup>18</sup>.

$$\text{TNT}_{\text{eqv.}} = \frac{\eta \Delta H_{\text{decomp}} * x_i V \rho}{300 \text{ kJ}} \quad \text{Eq. 16}$$

This incorporates the amount of reactive liquid in the unit but can be changed for the gas phase energy for explosion damage. The distance that will be used for the damage estimate will be 15 meters which is the minimum distance recommended by the CCPS of process equipment from safety equipment<sup>24</sup>. This is correlated to a maximum

overpressure,  $p_o$ , at this distance,  $r$ , using a correlation using a scaled distance as shown below<sup>18</sup>.

$$z_e = \frac{r[\text{m}]}{(\text{TNT}_{\text{eqv.}}[\text{kg}])^{1/3}} \quad \text{Eq. 17}$$

$$\frac{p_o}{p_a} = \frac{1616 \left[ 1 + \left( \frac{z_e}{4.5} \right)^2 \right]}{\sqrt{1 + \left( \frac{z_e}{0.048} \right)^2} \sqrt{1 + \left( \frac{z_e}{0.32} \right)^2} \sqrt{1 + \left( \frac{z_e}{1.35} \right)^2}} \quad \text{Eq. 18}$$

The outside pressure,  $p_a$ , is taken to be 1 atm and all the denominators of the scaled distance are in  $\text{kg}^{1/3}/\text{m}$ . To translate this overpressure to an endpoint, a probit calculation will be used for small equipment damage which is a good model for relief valves or emergency switches<sup>25</sup>.

$$Y = -23.8 + 2.92 \ln(p_o)$$

$$\%_{\text{affected}} = 50 \left[ 1 + \frac{Y - 5}{|Y - 5|} \operatorname{erf} \left( \frac{|Y - 5|}{\sqrt{2}} \right) \right] \quad \text{Eq. 19}$$

Half of the equipment being destroyed is taken as the dangerous value as shown below. This formulation and its constants will be used every time available energy is used or an overpressure calculated.

$$\text{Chem}_{\text{Exp. Damage}} = \frac{\%_{\text{Affected}}}{50\%} \quad \text{Eq. 20}$$

### 5.2.7 Explosion

In the original index there was an index called “fire/explosion” that has been split up for this index. Right now, estimating this parameter in a quick and easy fashion is in fledgling state. The assessment of chemical specific explosion hazards is confined to two ends of the information spectrum. At one end you have cutting edge QSAR research using the highest order molecular descriptors that today’s computers can barely handle. The other end references known experience through DOT classification and in the SDS.

Probabilities of a mechanical explosion and BLEVEs will be assessed later since they become much clearer with an approach that is not chemical specific.

For a chemical specific approach, physical properties will be used to classify how easily an explosion can develop from a fire. There are two areas that are important for fire propagation; the reaction front and the pressure front. The reaction front is where the combustion reaction happens in a fire. This moves at a rate depending on flammability regions and the availability of fuel in terms of mass transfer. Ahead of the reaction front, the pressure front is an area of high pressure caused as the reaction front pushes the surroundings. In fires, these fronts are far apart in space with a time delay. In an explosion, these two fronts are pressed on top of each other. This increases the efficiency of the reaction with the availability of reactants due to the pressure wave. In turn, the pressure wave increases drastically in overpressure due to the reaction front being more intense and the removal of the loss of pressure due to dissipation between the two fronts. The mechanics of these two fronts can be estimated to see if an explosion is a legitimate worry.

The first way to do this is the relative speeds of the fronts. With some space to build up power, this speed can turn a regular fire into an explosion. This value done in isolation at standard conditions is called the fundamental burning velocity,  $S_u$ , which is a chemical specific value. This usually comes from experiments and can be found from the NFPA <sup>26</sup>, or from the literature <sup>27</sup> for a select number chemicals.

$$\text{Chem}_{\text{Explosion}} = \frac{S_u}{45 \text{ cm/s}} - 1 \quad \text{Eq. 21}$$

The velocity of propane at 45 cm/sec (rounded off from 46 cm/sec) is used as a safe quantity with an index value of 0. There is a big division around 90 cm/sec between common explosive chemicals and chemicals manufactured as explosives so it will be used as the dangerous value. This would give aluminum dust a 1 on the index while would give the threshold for “fast” burning chemicals at 60 cm/s a value of 0.33 <sup>28</sup>.

Other than speed, the energy in the explosion,  $\Delta H_{\text{Exp}}$ , is a factor. How much drive the fire has to turn into an explosion as well as the power when it becomes an explosion can represent the explosibility of the chemical. This is calculated as the difference between the bond energies ahead of the reaction front and behind the reaction front. Most of the time there are more than one reaction occurring in these reaction fronts due to instability. The bond energies are then corrected using the available chemical energy. The formation of gases or prevalent side reactions can also lower this variables explanatory power. Availability of this variable is limited to chemical by chemical literature experiments and some aggregated lists<sup>18</sup>. The formula to turn this energy into an index is the same as in section 5.2.6.

The useful bridges between the spectrum of experimental studies and quantum mechanical models that allow for some predictability often require careful use. Often research in this field is limited to one functional group or one type of bond in an effort to help those in the field that are handling that specific chemical. One useful relationship is the oxygen balance as shown below where  $X$ ,  $Y$ , and  $Z$  are the number of carbon, hydrogen and oxygen respectfully<sup>29</sup>.

$$\text{OxyBalance} = \frac{[-1600\text{gm/mol}(2X + Y/2 - Z)]}{MW[\text{gm/mol}]} \quad \text{Eq. 22}$$

Most explosives utilize unstable redox reactions. If the combustion reaction has all the oxygen atoms in the form of carbon dioxide and water in the products then you can say the chemical is oxygen balanced. If the reaction requires oxygen atoms on the reactant side than it is said to be oxygen-deficient and has a negative oxygen balance. The efficiency of the reaction is the greatest in oxygen balanced chemicals without the worry of incomplete combustion (negative oxygen balance) or dilution of the reactants (positive oxygen balance). This is transferred to an index as shown below.

$$\text{Chem}_{\text{Explosion}} = \begin{cases} 2 - \frac{\text{OxyBalance}}{80} & , \text{for OxyBalance} > 0 \\ 2 + \frac{\text{OxyBalance}}{120} & , \text{for OxyBalance} < 0 \end{cases} \quad \text{Eq. 23}$$

This comes from the classical hazard rankings for oxygen balance with the high hazard region being centered on zero and asymmetrically lowers away from zero. When this function is sent through the constraint of values being between 0 and 1, this ranking is reflected. The asymmetry is because a lot of explosives have negative oxygen balances due to tight 3-d structure or other instabilities in their structure <sup>18</sup>.

However, many chemicals like oxygen and carbon dioxide are themselves oxygen balanced but are inert in terms of explosion energy. This also ignores isomerism which could have a large effect on explosive energy. Compounds without oxygen often produce negative balances no matter the explosive ability. To combat these problems the index will only use oxygen with weak bonds, or available oxygen, and will only be applied when the chemical has all four of the elements, C, H, N, and O. Isomerism needs to be checked with a higher order QSAR function if applicable <sup>29</sup>.

#### 5.2.8 Irritation

The second most common entryway for harmful chemicals in an industrial environment is absorption through the skin. The best case scenario would be LD<sub>50</sub> for a dermal route of entry for a rat on a 48 hour period. Some of this data can be found with EPAs EcoTox database <sup>17</sup>, the SDS or academic papers.

$$\text{Chem}_{\text{Irr}} = 1 - 0.5 \log_{10} \left( \frac{LD_{50, \text{Derm}}}{100 \text{ppm}} \right) \quad \text{Eq. 24}$$

This follows the same formulation as the LD<sub>50</sub> for inhalation in section 5.2.4. This is because for this index, the mass transfer differences between the two routes are similar enough to be put on the same scale.

In the absence of this data, pH is a good substitute using the formula from the original index below to capture acidic and basic substances.

$$\text{Chem}_{\text{Irr}} = \frac{|\text{pH} - 7| - 2}{5} \quad \text{Eq. 25}$$

If the substance is neutral it still can be an irritant which will be on the DOT label as well as on the hazards on the SDS.

#### 5.2.9 Chronic toxicity

For the long term effects of exposures, the main descriptor is the Threshold limit value -Time weighted average (TLV-TWA). This is a measure of the maximum amount of exposure a worker can receive in an 8 hour work day, every day of work without adverse chronic effects. The best place for this would be ACGIH which updates their numbers regularly with new data and with changing risk attitudes. Both the values can usually be found on the SDS if they exist.

$$\text{Chem}_{\text{ChronicTox}} = 1 - \frac{\log_{10}(\text{TLV} - \text{TWA})}{3} \quad \text{Eq. 26}$$

This comes from the idea that after 1,000 ppm the TLV-TWA value is not that useful because it is such a large exposure for such a long time. At this point, the constant loss of product is more of a worry than the health aspects. For chemicals that do not have this, the TEST output can generate preliminary toxicology data.

#### 5.2.10 Water effects

The ecosystem of a body of water will be broken up into three different classes, large organisms, small organisms and bacteria scale organisms. This area of study is rather healthy with a large amount of toxicology studies rapidly available for many different exposure times and different test organisms. The variables tested in each case are lethal concentrations in the water,  $\text{LC}_{50}$  for the large organisms and small organisms and the inhibited growth of the bacteria,  $\text{IGC}_{50}$ . If a plant site is known, then a representative from the local habitat could be used for the three different organisms. The organisms that are used by default to assess a wide variety of situations are Fathead minnow for large organisms, *Daphnia magna* for small organisms and *Tetrahymena pyriformis* for bacteria. The vast amount of data on this can be searched using the

EcoTox database but the TEST software automatically checks for experimental data from this database along with a QSAR estimate for the chemicals without much data<sup>13,17</sup>. The predicted value for the QSAR is  $-\log_{10}(\text{LC}_{50})$  with the concentration in molarity rather than ppm so this value should be held together to preserve the regression. Below is the formulation for all the three values.

$$\text{Chem}_{\text{Water effects}} = \frac{-\log_{10}(\text{LC}_{50})}{5} \quad \text{Eq. 27}$$

$10^{-5}$  M seemed to be a reachable quantity in the local environment so it was used as a dangerous quantity. Other important parameters that are used in these variables' absence are the existence of the DOT label for aquatic hazards, the H-codes in the SDS and the pH.

#### 5.2.11 Air effects

The air effects face the same conundrum as water effects but have a proxy parameter that can be consulted; chronic toxicity. Here more environmentally focused values can be chosen like the ERPG-2 (Emergency response planning guidelines) from the AIHA or the RfD (reference dose of no ill effects on an entire population) from the EPA from their toxicity fact sheets.

$$\text{Chem}_{\text{Air effects}} = 1 - (1/3)\log_{10}\left(\frac{\text{ERPG} - 2}{5 \text{ ppm}}\right) \quad \text{Eq. 28}$$

$$\text{Chem}_{\text{Air effects}} = 1 - (1/3)\log_{10}(\text{RfD}) \quad \text{Eq. 29}$$

The difference between these two values is that the ERPG is the concentration in the air that could cause a harmful effect on the population measured in ppm while the RfD is a dose per weight of the person for a specific time period that above which would cause harmful effects to the population, measured in mg/kg/day. The overall formulation comes from the chronic toxicity from air in section 5.2.9. Since the concentration would



have to be higher to end up being a threat to a whole population, a factor of 1/5 is given to the ERPG to put it on the same scale while the RfD would be on the same order of magnitude because of the use of dose.

Dispersion effects that were not a large factor for the danger to workers, take over in this setting because exposure to the public is on a different time and length scale. Here variables like the density of buildings around the plant or the wind patterns can be used in the future to get an estimate the hazards of a gas exposure.

#### 5.2.12 Solid effects

This will be done on a case by case basis if there are significant solid hazards to the environment. The first concern is in particle size being in the range to pass through a human's lung cavities and get to the alveoli at around 5-10 micrometers. This is also small enough to pass through many of the environment's filtration systems like soil sedimentation.

#### 5.2.13 Bioaccumulation

Up until now, the index was focused on the toxin's effect on the environment. The environment has many processes to regulate toxic substances, clean itself out and intensify certain chemicals. The ability of the chemical to evade these processes can be dangerous by itself. The next two parameters tries to take into account the relative amount and the time scale that the toxin is in the environment. One can imagine a situation where some chemical is released in a lake at a relatively harmless level. The chemical is absorbed in the kelp to the point where the kelp has a higher concentration. A fish eats the kelp and over time, the concentration in its body goes beyond his threshold level and it begins to destroy its organs. The concentration in the water is still below the level of organ failure but the chemical increased concentration through the food cycle. This was a big problem during the DDT pesticide epidemic as the DDT was

sprayed right below the point of irreparable damage but it accumulated through the food cycle and destroyed many ecosystems.

There are two parts to this phenomenon; the increase in concentration through the food chain (biomagnification) and the increase in concentration due to intake and storage of a prolonged release (bioconcentration). The first factor is a function of the local ecosystem which for now is set to be constant. To quantify bioconcentration, a mass balance is done on an organism. The inlet is from respiration and absorption, the output is secretion and the consumption is the metabolism of the organism. An inlet of food and water is a part of the biomagnification problem formulation which is set to be constant. A low bioaccumulation potential would be if the outlet concentration is close to the inlet. Bioconcentration factor (*BCF*) is defined as the ratio between the concentrations inside and outside the organism at steady state. This can either be from a real study in the ecosystem of choice, or predicted from a QSAR procedure. This factor often is not found unless it is a major pollutant, but the QSAR procedure is simple with the TEST software<sup>13</sup>.

$$\text{Chem}_{\text{Bioacc}} = 0.5 * \log_{10}(BCF_i) - 1 \quad \text{Eq. 30}$$

Some absorption will happen but classical interpretations on *BCF* is that having a *BCF* >5000 is the tipping point for dangerous propagation that will surely increase with biomagnification. To allow for even more toxic substances in the specialty industry it will be given a value of around 0.85 which results in the simple 0.5 factor out front with the subtraction by one to get rid of the inaccurate yet benign range below a  $\log_{10}(BCF)$  of two<sup>30</sup>.

Another value that can be used is the octanol water partition coefficient or  $K_{ow}$ . This is the ratio of the concentration of the chemical across a water octanol liquid-liquid interface. The absorption through a diffusion process between water and a substitute for plant matter (Octanol) can gain insights on how the chemical accumulates through equilibrium process. The problem is that it is highly affected by the solubility of the chemical and that such an equilibrium process does not represent the living organism interacting with the environment. This value simplifies the mass balance by assuming

the metabolism is not a worry. However, some chemicals are not metabolized well in organisms which would show up in the *BCF* but not with the  $K_{ow}$ . The advantage to using the  $K_{ow}$  is that the experiment can be easily setup in a lab and can gain valuable insights into the system. There is also a major effort to find a sensible relationship between the *BCF* and  $K_{ow}$ . This can also be estimated using the TEST software but this value would be the least reliable.

$$\text{Chem}_{\text{Bioacc}} = 0.5 * \log_{10}(K_{ow}) - 1.5 \quad \text{Eq. 31}$$

This follows the same explanation as the *BCF* but with more uncertainty in the lower end which leads to the 1.5 subtraction.

#### 5.2.14 Degradation

This parameter looks at how long a chemical remains in the environment after the exposure. How much it naturally degrades and how much the environment can degrade it are the two prominent factors determining degradation. If it does not degrade, then it can affect more ecosystems by passing through various natural cycles or transport systems (rivers). The primary variable is the chemical's persistency which is the half-life of a chemical tested in an environment. This variable depends heavily on the local environment so future work is to incorporate local soil types and algae that can or cannot break down the chemical. This info can be found with a search in the EcoTox database which has many studies and predicted persistency measurements from academia and practice<sup>17</sup>. The other value of note is half-life which only studies half of the problem at hand. If these values are not available they can be estimated from the TEST software<sup>13</sup>. These are then turned into an index as shown below.

$$\text{Chem}_{\text{Degredation}} = 0.5 * \log_{10}(\text{Persistency}) \quad \text{Eq. 32}$$

$$\text{Chem}_{\text{Degredation}} = 0.5 * \log_{10}(t_{1/2}) \quad \text{Eq. 33}$$

The reasoning behind the numbers is linked to the timescale of ecological processes. The water cycle is a main source of natural cleaning and degradation by having the toxins in the soil exposed to microbes, physical separation through a packed

“column”, and time for it to degrade on its own. Many times the age of wells range from dozens of days and then quickly drops off to months and years. The older the well the cleaner and safer the source is from pollutants. If a chemical degrades on the timescale of then it could get into our water supply and the water supply of other animals <sup>31</sup>. To make it simple 100 days was chosen by Koller et al. for a dangerous property and 10 resulting in a multiplier of one half <sup>1</sup>.

### 5.3 Secondary effects method, *Sec.Eff*, parameter-parameter interactions

The parameters themselves could have effects on other parameters like a fire leading to an explosion resulting in higher values for both. Additionally some of the information about the chemicals may not be captured with just the chemical values like toxicity values stipulating one mode of intake. This is when the *Secondary effects* method is used to make the Effective Dangerous Properties (EDP) as shown below. Design variables in this stage do not have that much sway over these methods so they are considered the chemical specific methods.

$$EDP_{para, chem} = IntVal_{para, chem} + SecEff_{para, chem} \quad \text{Eq. 34}$$

This method is the result of the original index’s fate index. The main driving force for the inclusion of this correction was to assess how the party is exposed after a loss of containment. Partially this is covered by the mobility parameter, which tries to assess the chemicals’ path and time scale after loss of containment. The other part of the equation is how much of the parameter gets transferred to the party exposed. Health data often requires this extra step because of the dependency on mode of exposure (inhalation as opposed to ingestion) as well as the classification of carcinogens. Mathematically, the way to represent this is with an if-then statement specifying the mode of transfer or specific release scenario. What is missing from the equation is then parameter-parameter interaction.

When something like explosion and fire hazards exist together it is a more dangerous situation since one can cause the other. This can be modeled with an “And” gate or certain parameters multiplied together. This requires a perspective looking at all

the parameters and the body of initial process safety information. This means it should exist as an additive factor applied on a chemical basis. Table 2 shows all the secondary effects used currently.

This factor does not have the explanatory power of a dangerous property at an index value of 1. This is a modifier for extra, exclusively dangerous information so its range will be from 0 to 0.5. The maximum of 0.5 should be given for a combination of two properties with an index value of 1 which results in a multiplier of 0.5 as shown below.

$$\text{SecEff}_{\text{para, chem}} = 0.5 * \text{SecEff}_{\text{para, chem}}^{\text{Raw}} \quad \text{Eq. 35}$$

**Table 2. The formulas and explanations for the secondary effects**

	Parameter	Secondary Effect	Reasoning
1	Mobility	0	-
2	Fire	Mobility*Fire	More areas that can be in a flammability region
3	Acute Toxicity	1.25*Mobility*Acute Toxicity	How quick the path from release to the workers is traversed greatly affects the danger (hence 1.25)
4	Probability of runaway	Expected Damage* Prob. of Runaway	risk = consequence * probability
5	Expected Damage	Expected Damage* Prob. of Runaway	risk = consequence * probability
6	Explosion	Mobility * Explosion	More areas that can be in an explosibility range
7	Irritation	Mobility* Irritation	Larger affected area on the victim and the mode of transport between the loss of containment and the victim
8	Chronic Toxicity	1.25*Mobility*Chronic Toxicity	How quick the path from release to the workers is traversed greatly affects the danger (hence 1.25)
9	Water effects	WaterEff * Bioacc * Degrad	Environmental consequences are affected by the chemicals ability to “survive” in the environment.

**Table 2. Continued.**

	Parameter	Secondary Effect	Reasoning
10	Air effects	AirEff * Bioacc * Degrad	Environmental consequences are affected by the chemicals ability to “survive” in the environment.
11	Solid effects	0	-
12	Bioaccumulation	0	-
13	Degradation	0	-

#### 5.4 Mixed method, *Mix*, chemical-chemical interactions

When collapsing the chemicals an assumption is used that there are no interactions between the different chemicals. This is checked by the *Mix* method which goes through the interactions between all the chemicals in the solution. The equations that make up *Mix* is a combination of parsing the output of the chemical reactivity worksheet, some mixed versions of the chemical equations, and dedicated models for interaction effects. As opposed to binary interactions, the preferred version of the equations used is solution based. This is done because binary interactions model a situation that does not exist in reality just like the previous methods. When this is added to the previous step it becomes the Mixed Dangerous Properties (MDP).

$$MDP_{para} = \sum_{\forall Chem} w * EDP_{para, chem} + Mix_{para} \quad \text{Eq. 36}$$

Where the  $w$  is the chosen weights for this aggregation either best case, worse case or an average. User weights can also be supplied and inserted here if more control is needed.

##### 5.4.1 Mobility

An indicator of how much interaction a mixture will have in dispersion modeling or diffusion is with the molecular weight. For many formulas, an influential input variable is molecular weight. If a mixture had similar molecular weights, they would not interact that much since these equations would see them as the same situation. Molecular

weight is also linearly related to the spherical radius of the molecule which is another important input variable.

This will be benchmarked against a hypothetical mixture with the same number of components all having a molecular weight of water. This mixture would be the easiest to disperse after a loss of contamination cause its small size and lack of interactions.

$$\text{Mix}_{\text{Mobility}} = \sqrt{\frac{\sum_{\forall \text{Chems}} \frac{1}{MW_i}}{\frac{\text{numChem}}{18 \text{gm/mol}}} - 1} \quad \text{Eq. 37}$$

Here the subtraction of 1 centers the index on 0 for a case that is as devoid of interaction as a mixture of water.

#### 5.4.2 Fire

One idea for this mixing factor is to incorporate the fire triangle. In terms of the probability of a fire, the ignition energy will be assumed to be present because there are so many ignition sources in a chemical plant. The existence of an oxidizer with a fuel can be disastrously dangerous while the existence of an inert agent or excess water can decrease the flammability. This is quantified by the existence of different groups using the CRW classification scheme. Their effect is weighted by their theoretical mole fraction in the vapor phase since combustion happens in the vapor phase.

$$\text{Mix}_{\text{Fire}} = 2 * \left[ \sum_{\forall \text{Chem}} y_i * B(\text{fuel}) \right] * \left[ \sum_{\forall \text{Chem}} y_i * B(\text{Oxidizer}) \right] \quad \text{Eq. 38}$$

The function B returns a Boolean value (0 for no and 1 for yes) for the given type of chemical. As it exist now, the index only predicts dangerous situations so the range of values are from 0 to 0.5 where .5 is where the entire vapor space is filled with half oxidizer and half fuel. This value is the worst possible situation and so the factor of 2 is out front to scale this dangerous value to 0.5. In the future the effect of water in the vapor phase will be added in to so a beneficial situation.

This introduces another problem with the LFL formulation. A fire is a combustion reaction in the vapor phase, so the only thing that matters is the vapor mole fraction of fuel and not the individual components in the liquid phase. A mixture LFL is then the amount of this fuel that is necessary to cause a fire and is calculated with Le Chatelier's equation as shown below.

$$LFL_{\text{Mix}} = \frac{1}{\sum_{\forall \text{Chem}} \frac{y_i}{LFL_i}} \quad \text{Eq. 39}$$

$$\text{Mix}_{\text{Fire}} = 0.5 - \frac{LFL_{\text{mix}}}{30 \text{ wt}\%} \quad \text{Eq. 40}$$

First the mole fraction is on a combustible basis or with only the combustible values included. This is already modified using the activity coefficient as calculated in Aspen. Translating this to an index comes from the regular index translation from the initial value version for *LFL*. The difference is that it is halved due to it being an additive factor. The reason that this is not used instead of the initial values is because of the assumptions used in this equation's proof. It assumes constant heat capacity, combustion kinetics for a chemical are the same as in the mixture and that the adiabatic temperature rise for all the components in the mixture are the same. This decreases its reliability to the point where it cannot be used as evidence to explain the full range of the index let alone explaining the fire hazards by itself. This is a reason why it is also an additive factor so it can be easily turned off and adjusted independently of the rest of the index.

These assumptions can be partially tested for a mixture and the deviations can be quantified within the mix index. If one of the assumptions is wrong that throws off other calculations in this section since these are the fundamentals behind fires. Many mixture correlations for this field try to marry the complex interaction between the different kinetics of the reaction with the thermodynamic changes. The formulation often uses Boiling point as a baseline with adjustments using chemical equilibrium, molecular structure and/or heats of reaction<sup>32</sup>. An effective heat of combustion can be calculated by weighting it with the mass fraction in the vapor phase using an activity adjusted Raoult's law. If this is correlated alone this can be used to isolate the effects of the heat



of reaction and chemical equilibrium from the effect of the different adiabatic temperatures and changes of heat capacities that are of a different nature<sup>18</sup>.

$$LFL_{\text{Mix}} = \frac{11.2 \text{ kcal/mol}}{\sum_{\forall \text{Chem}} y_i \Delta H_{\text{burn},i}} * 100\% \quad \text{Eq. 41}$$

Without this index, the LFLs would be simply averaged or the worst case scenario would be used. The effect of these assumptions can be gauged with the average case to see how much of a worry the assumptions are.

$$\text{Mix}_{\text{Fire}} = \frac{LFL_{\text{mix}} - \text{mean}_{\text{chem}}(LFL_i)}{5 \text{ wt \%}} \quad \text{Eq. 42}$$

A change of 5 wt% in the LFL would signify a major breach of the assumptions which would throw off the previous calculations. This formulation allows aggregation of the *Chem* with *Mix* to follow the same arithmetic as the analytical formulas with the ability to change their impact with the human assessment of the data sources.

#### 5.4.3 Toxicity

The same principle for fires applies to both toxicity measurements. The thing that matters for a human's defense mechanism is the relative amount of toxins that it has to filter. In this way we have the idea of overexposure using a similar formula as the Le Chatelier's equation.

$$\text{Exposure} = \sum_{\forall \text{Chem}} \frac{C_i / 500 \text{ ppm}}{TLV_i} \quad \text{Eq. 43}$$

Here a value over one is said to be an overexposed worker and not in compliance with the given regulation or recommendation. Normally, the 500 would not be there but this is a scaling factor for the concentration that a worker is exposed to given the concentration in the unit. This procedure can be done with most toxicity measures except the  $LD_{50}$  data. As a correction factor this will be centered on zero and halved with the formulation below.

$$\text{Mix}_{\text{Tox}} = 0.5 * (\text{Exposure} - 1) \quad \text{Eq. 44}$$

The subtraction is to center the value on the regulation. The 0.5 is due to the using calculated values and the conversion from unit concentration to exposure.

#### 5.4.4 Probability of a runaway reaction

As we can now see all the chemicals and their relative amounts, the likelihood of an initiating event for a runaway can be assessed. If all the reactions were known a combination of the kinetics and thermodynamics could be used to rack the potential for a runaway reaction. Here the amount of reactants needed, resilience of the reaction to the presence of other chemicals or situations as well as the amount product gas produced per reactant and other secondary properties could be measured for the whole set of reactions that could possibly occur using all the possible chemicals and concentrations that could be present. The result would include a list of specific sensitive properties that can be tracked and controlled in the next design phase rather than after a HAZOP review.

This ideal can toned down so it can be realized thanks to molecular predictions and software packages like the Chemical Reactivity Worksheet (CRW)<sup>12</sup>. This program is a simplified, repurposed and free version of the CHEETAH<sup>33</sup> program that estimates potential reactions and their thermodynamics using the Benson method. This is not a full molecular model like a QSAR model but breaks the molecule into significant parts. Partially this breaks down along functional group lines with the other division being along weak, reactive or structurally important bonds. The thermodynamic effects and contributions of these fragments are used to calculate things like Gibbs free energy of formation and heat of combustion. These can be done using ASPEN's property estimation techniques for lower temperatures while this is useful till 1500°C. Applied to reactions, this approach can be used to estimate the Arrhenius factor and activation energy as well as heat of reaction. The CRW conduit allows for the batch checking of a mixture for such reactions. The output is translated into two main categories for negative outcomes: immediate reactivity hazards and evolved gasses. For reactivity hazards, things like corrosivity, heat generation and explosive ability is assessed while the potential gases produced during a reaction are compiled for a reaction pair.

To turn this into a mixing factor these need to be transferred to the program in a way that is consistent with the index as a whole. The index will see the CRW results through a procedurally generated output report file outlining the documentation and the immediate results of the test. These are compiled by CRW into large categories of “compatible”, “caution” and “not compatible”. However, this will not be used since the documentation itself can give more insight and a larger range of values. There are two different pieces of information that will be lifted from the text files; the chemical reactivity and the potential released gases. Each of these will be stored in the form of a half triangular matrix with the rows and columns being the list of all the chemicals in the entire plant. To compute the final value they will be summed up as follows:

$$\text{Mix}_{\text{ProbRun}} = \frac{\left( \sum_{i=\forall(\text{chem} \in \text{Unit})} \sum_{j=\forall(\text{chem} \in \text{Unit})} (\text{ReactMat}(i, j) + \text{GasMat}(i, j)) \right)}{\text{Num}(\text{pairs})} - 0.1 \quad \text{Eq. 45}$$

The two summations are targeting all the chemical pairs that exist in that one unit. This is divided by the number of pairs to get an average value of items. The expected value of items for an innocuous pairing was determined to be 0.1 due to the inclusion of items that are only applicable at unstable conditions. This was done by a qualitative look at the chemical database but a future quantitative statistical survey can be done.

To create the master matrix for the Reaction and gas matrixes, the items in each of the pairs’ reports are summed up. For chemical hazards the number is multiplied by the severity of the language used. If an item has words like “Intense” and “Explosive” For the hazards guidewords that are used like “Intense”, will augment the items in the report. For the gas matrix, each potential produced gas will give a nominal value of 0.1. The value of one pair cannot exceed 0.5 due to unstable mixtures often outputting matches at extreme conditions.

#### 5.4.5 Explosion

One way to check the mixture properties for explosions is through a mixture burning velocity. Usually the fundamental burning velocity is found by changing the composition of fuel and air to get different flame speeds. The most efficient burning is at the stoichiometric amount of fuel to air. How close the fuel to air mixture is to this value is normalized as the equivalence ratio. This is done on a mass basis as shown below.

$$\phi = \frac{m_{\text{fuel}} / m_{\text{oxidizer}}}{(m_{\text{fuel}} / m_{\text{oxidizer}})_{\text{Opt}}} \quad \text{Eq. 46}$$

The amount of fuel follows a parabolic shape with the burning velocity with the peak being around the stoichiometric ratio. To take the fundamental burning velocity and change it according to the given equivalence ratio is a useful correlation. This is done through the temperature and pressure dependence exponent as shown below<sup>34,35</sup>.

$$\begin{aligned} S_u &= S_{u,o} * \left( \frac{T}{T_o} \right)^\alpha \left( \frac{P}{P_o} \right)^\beta \\ \alpha &= 1.783 - 0.375 * (\phi - 1) \\ \beta &= -0.17 * \phi^{0.5 * \text{sign}(\phi)} \end{aligned} \quad \text{Eq. 47}$$

The nominal value of temperature and pressure,  $T_o$ ,  $P_o$ , are the conditions that the database value of the burning velocity was measured in. Either this will be user inputted from the specific data source or they will be assumed to be standard conditions. The initial formula is often used in studies to find the specific alpha and beta for their specific system. This is just a correlation for the effect of the equivalence ratio when in reality it depends on many equipment specific factors. To see the mixture effects, this formula is enough.

To make a mixture burning velocity the individual velocities will be weighted by their composition in the vapor phase after adjusting for temperature and pressure. The optimal fuel to air ratio is chemical specific because the chemical would burn better if the air was stoichiometric for their specific combustion reaction. To see how the mixture should affect the velocity and to use the most conservative value, the mixture fuel to air ratio of a hypothetical release will be the optimal for the mixture. This will be calculated

using a hypothetical fuel with all the chemicals that could be fuels being treated as one chemical.

$$S_{u,Mix} = \sum_{\forall \text{Fuels}} S_{u,o,i} * \left( \frac{T}{T_{o,i}} \right)^{\alpha_i} \left( \frac{P}{P_{o,i}} \right)^{\beta_i} \quad \text{Eq. 48}$$

The subscripts on alpha and beta are from the change in equivalence ratio with the changing optimum fuel ratio. This is turned into a mixing index as follows.

$$\text{Mix}_{\text{Explosion}} = \frac{S_{u,mix} - \text{mean}_{\text{chem}}(S_u)}{50 \text{ cm/s}} \quad \text{Eq. 49}$$

This comes from applying the slope from the equation for the chemical specific burning velocity as shown in section 5.2.7 to the change in the burning velocity due to mixing. Hopefully this will assess how each chemical is affected by the other in terms of inerting and the changes in process conditions.

As a mixture, the explosion hazard that can be assessed is a BLEVE or Boiling liquid expanding vapor explosion. Heating or a loss of pressure may cause the liquid to start to boil. With a large change in heat capacity of the liquid and gas state the vessel begin to weaken as the pressure of the vapor grows. The latent heat of vaporization and the increased pressure causes more boiling in a positive feedback loop. Eventually a rupture occurs in the vessel and can cause an explosion. This can be better assessed here with the ability to look at the mixed properties.

The liquid is flashing up in a BLEVE do to the design pressure or a decreased pressure due to expansion or a loss of containment. Using a system with one mole of the mixture and solving the component mass balance comes to the following equation. The definition of the  $K$ -value is used as  $y/x$  as well as the physical limitation that the summation of the vapor mole fraction has to equal one<sup>19</sup>.

$$1 = \sum_{\forall \text{Chem}} \frac{z_i K_i}{1 + f_v (K_i - 1)} \quad \text{Eq. 50}$$

The value of  $f_v$  can be found through a root finding procedure or iteration through guess and check to get the value for the mixture. The new amount in the vapor phase can be found using the old amount added to this amount vaporized. This results in a new

pressure that can be found with the ideal gas law or using the compressibility factor. The energy that would be released if this were allowed to expand isothermally is shown below. An isothermal expansion is chosen because it is the most conservative estimate and the process can be assumed to be fast.

$$E = P_{\text{Flash}} V \left( \ln \frac{P_{\text{Flash}}}{P_0} \right) \quad \text{Eq. 51}$$

$$\text{Mix}_{\text{Explosion}} = 0.9 * \log_{10}(E / 24\text{kJ}) - 1 \quad \text{Eq. 52}$$

This value comes from doubling the range of available energy in section 5.2.6 and then centering the value on zero.

## 5.5 Vessel method, *Vessel*, unit-process interactions

### 5.5.1 Overview

The solution is then placed in a process unit that has an assumption that it will never break down or lose containment. The *Vessel* method goes through a risk assessment for a loss of containment in each of the scenarios outlined by the parameters. This looks at the perspective of the maintenance personnel trying to understand which units would need more care due to the physical makeup of the unit as well as the process in the unit. A main addition to this area is the model alteration capability. This allows a designer to add things into the design that is not captured in the ASPEN design. These will be assessed in terms of their effect on the detection capabilities of the system, the failure rate or mitigation of the parameters directly. This system is flexible enough to cover everything from process control to end of the pipe technologies to more rugged material of construction.

The final *Vessel* will be calculated by using a risk criticality index<sup>36</sup>. This falls under the idea of an increasing model complexity as the index reaches its final stages. The index combines the consequence analysis with the frequency of the event and how often it will be detected as follows.

$$\text{Vessel} = \text{LossCont} * \text{Detection} * \text{Consequence} \quad \text{Eq. 53}$$

The probability of a loss of containment ( $P_{\text{LossCmt}}$ ) will be an adjusted failure rate from a nominal failure rate for every ASPEN model. It will be adjusted like a unit conversion calculation with the base failure rate having units of “standard process conditions” and “without any alterations”. The formula to get this is as follows.

$$P_{\text{LossCmt}} = f_{\text{Base}} * \Delta f_{\text{model}} * \Delta f_{\text{process}} \quad \text{Eq. 54}$$

To turn this final failure rate in units of hr-1 into a unitless additive factor, a logarithmic scheme is used with a dangerous failure rate of  $1*10^{-2}$  hr-1 and a benign failure rate of  $1*10^{-5}$  hr-1.

$$\text{LossCont} = \frac{1}{3} \log_{10}(f * 10^5) \quad \text{Eq. 55}$$

The extremity of the process conditions will be assessed in  $\Delta f_{\text{process}}$  while the model alterations effect on failure rate will be assessed in  $\Delta f_{\text{model}}$ . The detection will be filled with nominal values for each parameter that can be adjusted by a model alteration. The consequence value will incorporate the consequence analysis from previous methods as well as the model alterations assessed in this method as shown below.

### 5.5.2 Process extremity

Extreme process conditions can cause fatigue in control systems and physical fatigue in the unit. To account for this deviation the effects of the most relevant process conditions, temperature and pressure, will be multiplied together to find the overall effect for the process.

$$\Delta f_{\text{Process}} = 10^{\left[ \frac{\text{Val}_T}{\tau_T} \right]} * 10^{\left[ \frac{\text{Val}_P}{\tau_P} \right]} \quad \text{Eq. 56}$$

Overall, this formulation is trying to make a linear line on a log scale by using the dangerous amount and quantity as second point with the ambient conditions. This allows the effects to be multiplied together into a value that is naturally centered on 1 and bounded at zero. For a unit conversation type of calculation, this is perfect and

interchangeable with more advanced fatigue models. More or less, this has been the procedure for the other indices but it has to be given a procedural process here due to the maximum failure rate changing with the function of the unit as designated by the unit's class. The exponent is normalizing a key variable for fatigue in the unit. *Val* comes from the model in particular and tau is how much of a dangerous quantity of that variable would change the failure rate.

For temperature, the model used is the distance away from an ambient temperature of 25°C. Each direction has its own maximum value to account for the greater effect of cryogenic temperatures on systems. For positive *Val*, the maximum is 600°C corresponding which would put the temperature of 500°C as the threshold for dangerous quantities at an index value of 0.8. For negative *Val*, the maximum is set to 125°C corresponding to a process temperature of -100°C, which is when there may be a significant amount of solids is something were to fail.

$$Val_T = \max(T - 25^\circ\text{C}, 25^\circ\text{C} - T) \quad \text{Eq. 57}$$

For pressure the variable used is the isothermal expansion of the contents of the units. This equation was used during the BLEVE calculations in section 5.4.5. Like before the isothermal expansion is used because it is the most conservative out of other methods like thermodynamic availability or adiabatic expansion. The difference in this formulation is that the expansion is between the design pressure and the atmospheric pressure. The maximum value differs for vacuum and pressurized vessels with 1000 kJ for a vacuum and 1000 mJ for any other vessel<sup>18</sup>.

$$Val_P = PV \left( \ln \frac{P}{P_{\text{atm}}} \right) \quad \text{Eq. 58}$$

The tau in Eq. 56 is the slope of the regression which can be found by the two failure rates and maximum value,  $Val_{\text{Max}}$ , which is defined by the model used. The two failure rates are the base failure rate,  $f_{\text{Base}}$ , and the maximum failure rate,  $f_{\text{Max}}$ . Below is the formulation for the tau of the process condition.



$$\tau = \frac{\log_{10}\left(\frac{f_{\text{Max}}}{f_{\text{Base}}}\right)}{Val_{\text{Max}}} \quad \text{Eq. 59}$$

The base failure rate is defined by the APSEN model selected. In some models this is defined by a design parameter like compressors' failure rate being defined by the horsepower requirement. The maximum failure rate for temperature and pressure is defined similarly using a few process conditions. The maximum failure rate for pressure is  $5 \times 10^{-6}/\text{hr}$  for pressurized vessels ( $P_a > 2\text{atm}$ ). A reactor would have a failure rate for  $50 \times 10^{-6}/\text{hr}$  for temperature and will be treated as a pressurized vessel for pressure. If these conditions are not met, then the maximum failure rate is  $100 \times 10^{-6}/\text{hr}$ .

The caveat to these calculations is that they are only for certain parameters. It does not make sense to do the calculations for a loss of containment when the scenario checked by the parameter does not depend on a loss of containment. An obvious example of this is Mobility that tests the distance and ease for the “hazard” to reach people or the community after loss of containment. In its definition, it is assumed a loss of containment already happened so testing for it would not be fair and would ultimately lead to double counting the different effects. The full list of calculations is shown in Table 4.

### 5.5.3 Model alterations

The idea of capturing data from vague ideas about what should be is at the forefront of incorporating all the information available and customizing an output to the designers' needs. A wide variety of needs, an incredibly low amount of hard numbers and a requirement for the adjustments to be able to swing risk assessments by orders of magnitude requires something different than the other methods' calculations.

To deal with this, a semi-quantitative risk assessment using a rubric is done on each of the proposed enhancements. First, the alteration is classified in how it helps the system in terms of changing the failure rate, detection or the mitigation of an event. This determines the goal of the unit and mathematically shows the program where to use the

result. It is then classified into the specific parameters or the dangerous conditions it protects against. For the maximum values, it would either affect the maximum temperature in determining the process extremity or the maximum pressure. For Detection and Consequence, these values effects one or more of the parameters. The designer then evaluates the system using a ranking scheme and a rubric in the categories of strength, maintainability, and reliability. This value is ubiquitous for many different types of systems so it is called Usefulness as shown below.

$$\text{Usefulness} = \text{Strength} * \text{Reliability} * \text{Maintainability} \text{ Eq. 60}$$

Strength is defined as how effective the equipment will be in the given task. Will it actually mitigate the effects of a fire or will it just warn of impending danger? Reliability is defined as how often someone has to repair or replace the system. Maintainability is defined here to be the ease of this repair or replacement in terms of amount of expertise required, length of down time, ease of acquiring the new parts and how easy it would be to access the part. These values get a value of 1 for an unhelpful situation and a 5 given for complete delivery of the definitions. The rubric is as shown below in Table 3.

**Table 3. Rubric for assigning alteration usefulness values**

Score	Strength	Reliability	Maintainability
1	Temp. relief or notification	MTTF ~1 month	Shutdown on order of months / esoteric parts / cramped quarters
5	State of the art control	MTTF ~5 years	Quick turnaround/ ubiquitous parts / easy access

This introduces a wealth of possibilities for the types of systems that can be included. An inherently safer solution would have the benefit of having high scores for maintainability and reliability but it still has to do its job. Alternatively, if the problem can be easily solved with another material of construction or a thicker hull, the system

would be able to see this in the same formulation. This area highlights how every method can be approached using an inherently safer approach or through a system level risk reduction point of view.

To translate this to an index value, one section was given for free with a useful value of 125 and a useless value of 1 which are simply the numerical bounds of the ranking system. This index is called Armor% because it is taken as a protection system while a value of 1 would mean total protection.

$$\text{Armor}\%_{\text{mode}} = \frac{\log_{10}(\text{Usefulness})}{\log_{10}(125)} \quad \text{Eq. 61}$$

The area that this armor protects against is determined by the initial characterization of its mode. There are four ways that an alterations can impact a unit; max, base, detection or consequence. Max is the maximum failure rate due to extreme processes, specified further as an extreme temperature or an extreme pressure or both. Base covers protections on the overall failure rate in normal operations. Both of these affect their respected failure rates in the same way as shown below,

$$f = (1 - \text{Armor}\%) * f_o \quad \text{Eq. 62}$$

where  $f_o$  is the original failure rate from the aspen model whether it be base, max temperature or max pressure.

Detection and mitigation can be applied to any of the parameters or multiple parameters and protects against values used in the overall *Vessel* risk assessment. A maximum value of 0.5 reduction in one parameter is allowed because it should not have a larger extent than a regular index since it is only fix and not necessarily fixing the inherent problem. One model should not be related or required for another model's execution. However, there are some small exceptions. The first one was in the *SecEff* that was dependent on the *Chem.* values and the Consequence calculation is another. The alteration directly changes the hazards calculated in the previous section by definition. This is what a user would think adding a stronger hull would do which far outweighs model purity. To help with model purity, the value to be used is the chemical hazards with a simple average of the chemicals. The thing that is important for this stage would

be the presence or absence of that hazard to be mitigated so this is done with a boolean check on a nominal value of 0.05 index units. The results are shown below.

$$\text{Consequence}_{\text{Para}} = B(\text{Chem}_{\text{Para}}^{\text{avg chem}} > 0.05) - 0.5 * \text{Armor}\%_{\text{Para}} \quad \text{Eq. 63}$$

Detection tests the administrative and process controls of a plant. If a designer thinks that a process will be easy to control or that the company will be moving their best talent to the job site, they can adjust for a better detection score. This is done in the same vein as Consequence as shown below.

$$\text{Detect}_{\text{para}}^{\text{Adj.}} = \text{Detect}_{\text{para}}^{\text{Base}} - 0.5 * \text{Armor}\%_{\text{Para}} \quad \text{Eq. 64}$$

The difference is in the base values which are now set as a nominal value instead of an average of previous results. These nominal values are posited values that are said to be representative of an average process control system and administrative protocols as shown in Table 4. For the base detection, a nominal value of 0.3 was given for composition monitoring it can be found out pretty easily with flow and space time in a reactor. The other parameters were adjusted to this base value by how easy it is to detect compared to composition.

**Table 4. The parameter dependence on the *Vessel* calculations**

Parameter	LossCont	Base Detection
Mobility	1	0.2
Fire	LossCont	0.4
Acute Toxicity	LossCont	0.3
Probability of runaway	1	0.1
Expected Damage	1	0.5
Explosion	LossCont	0.2
Irritation	1	0.3
Chronic Toxicity	1	0.2
Water effects	LossCont	0.3
Air Effects	LossCont	0.3
Solid effects	LossCont	0.7
Bioaccumulation	LossCont	0.3
Degradation	LossCont	0.3

## 5.6 Hot spot method, *HotSpot*, changing conditions' effect

Up until now, one condition was used in to assess all the methods. For a reactor, a litany of properties is changing and some chemicals may even be emerging from the solution. These dynamics need to be captured by the system to accurately judge a unit over whole length of the unit. This is done in the method, *HotSpot* that redoes the index (up until a CDP) for the different conditions found in an along the length of the unit. The variables that are changed are the ones that the function of the unit changes. A heater is designed to change the temperature of the process so Temperature and all other variables that change with temperature will be available for the iteration. The locations that are available for iteration are called “Spots” and are the inlet and outlet areas as well as a spot in the middle or a representative spot for an average or steady state value. A safety expert would try to use this last value in detailed calculations. Taking the error between this calculation and if the safety expert explicitly took the conditions at all the inlet and outlets into account results in the *HotSpot* quantity as shown below. This evaluates the effect of taking into consideration the changing conditions along the length of the unit which was an assumption that was in place throughout the previous calculations. In the future, more conditions could be tracked and more middle points could be examined.

$$\text{HotSpot}_{para} = \frac{\sum_{\forall \text{Changing Vars}} \sum_{\forall \text{Spots}} \text{CDP}_{para}(\text{Spot}, \text{changing var})}{\text{num}(\text{Spots}) * \text{num}(\text{changing Vars})} - \text{CDP}_{para}(\text{avg or steady state})$$

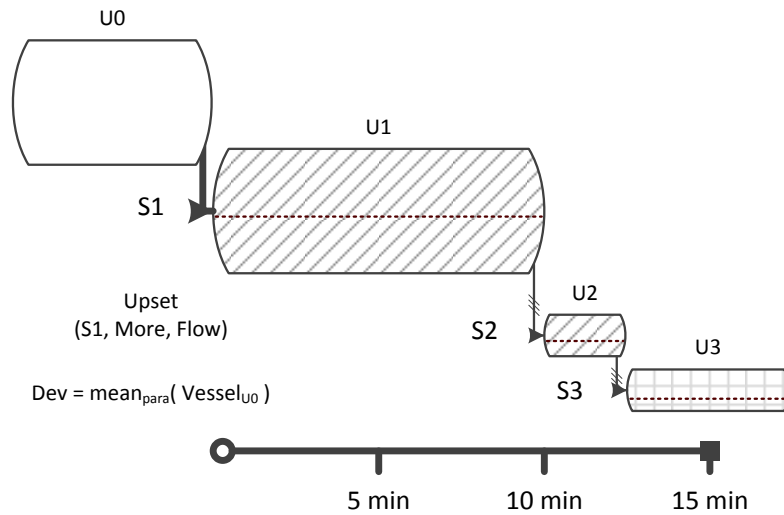
**Eq. 65**

This is done one condition at a time, keeping the rest of the values at the nominal value. This method is added to the CDP to become the final unit-dependent value, named Unit Dangerous Properties (UDP).

## 5.7 Unit-unit interactions, *Unit-Unit*

The units are collapsed with the assumption that the units are not affected by each other. This is tested in the method *Unit-Unit* that tries to take the perspective of a HazOp team evaluating upset conditions. There are two parts of this problem: process

control and abnormal event mitigation. Both are shown in Figure 2 as the model generates different upsets using HazOp methodology and then assess how well the downstream units handle the upset. To pick a scenario a variable (currently T,P,F) and guidewords (currently more and less) are chosen. The guide word is given a multiplier integer (-1 for less, etc.) and the deviation is calculated.



**Figure 2. The model of an upset condition for the Unit-Unit interaction calculation is shown. The slashed lines represent a change in the stream while the bold lines indicate an increase in flow. A clear background represents the normal conditions, diagonal lines represent a full upset throughout the unit and the grid represents a partial upset.**

This deviation value is the expected propensity of fluctuations in the conditions at the inlet of the upset unit. This can be inferred from the failure rate data, which is already estimated by the upstream unit's *Vessel* average value. This brings upset formulation from the realm of painful enumeration in real time in front of a group of thinly bound group of professionals to automatic and arguable science. This is done as the deviation amount for the variable of choice as shown below.

$$\text{Dev} = \left[ \text{mean}_{\text{para}} (\text{Vessel}_{\text{unit l}}) \right] \quad \text{Eq. 66}$$

The resulting 15 minute upset (from RMP regulations) will be calculated and the all the conditions of the downstream unit could potentially change. If the downstream unit has a residence time that is smaller than 15 minutes, the upset continues to the next unit. The calculated process conditions at the outlet of the first upsetted unit travels to the next unit as an upset. This continues until the 15 minutes are finished or the upset recycles back on itself. Formulaically, *Unit-Unit* will be the summation of all the units' difference between the upset conditions and the normal conditions. Effectively this is only relevant for those units that are directly upsetted by the upset. This can be used as a measure of the robustness of the system to an upset in that stream.

$$\text{UUval}_{s,g,v,para} = \sum_{\forall \text{Units}} \text{CDP}_{para}^{\text{Unit } x} (\text{Upset}_{s,g,v}) - \text{CDP}_{para}^{\text{Unit } x} (\text{normal}) \quad \text{Eq. 67}$$

This is done for all the guidewords,  $g$  (currently more and less) and all variables,  $v$  (currently T,P,F). This will be averaged together to get the final *Unit-Unit* value for each of the parameters in that stream,  $s$ , as shown below.

$$\text{UnitUnit}_{para} = \frac{\sum_{\forall g} \sum_{\forall v} \text{UUval}_{s,g,v,para}}{\text{num}(g) * \text{num}(v)} \quad \text{Eq. 68}$$

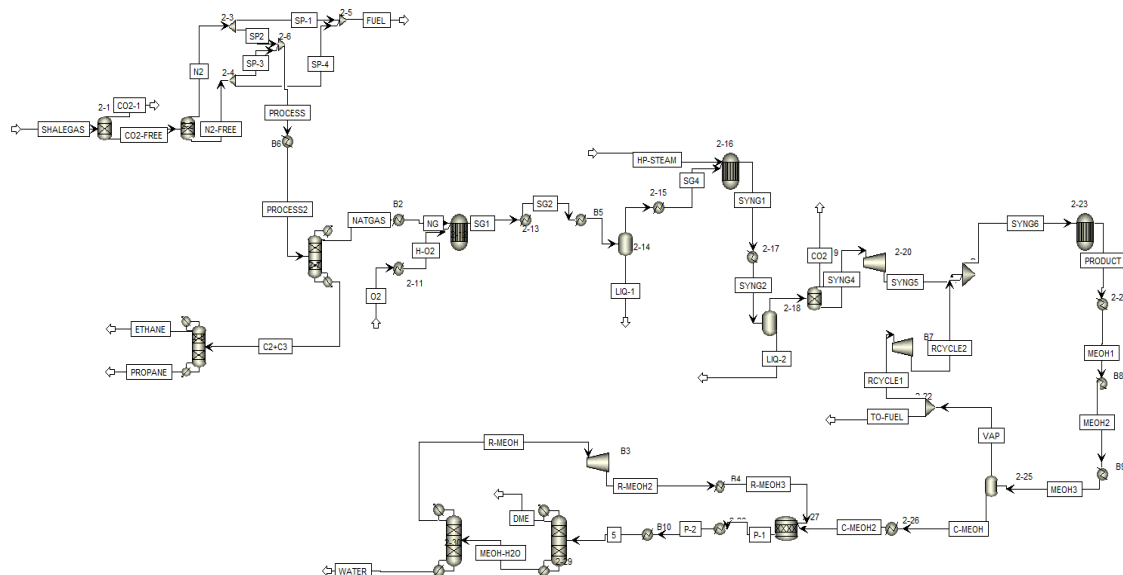
This is done for all the streams in the plant and aggregated together when the unit dimensions is collapsed. Once this is added to the combined version of UDP, the dangerous property is said to be representative of a system wide approach to the plant and is said to be an Integrated Dangerous Properties (IDP).



## 6 APPLICATIONS\*

### 6.1 Case study description

The index was applied to a 550 million pounds per year dimethyl ether (DME) production facility from shale gas design. The flowsheet and simulation results are based on recent research work by Karagöz<sup>37</sup>. The ASPEN Plus flowsheet is shown in Figure 3. This can be taken as a cutting edge, grassroots design that would have taken a HazOp team or a safety expert longer to understand and go through.



**Figure 3. The PFD for the DME production plant used as a case study for the IEHS index<sup>37</sup>**

\* The case study's data was used with permission from Karagöz, S. *M.S. Thesis*; Thesis; Texas A&M University: College Station, TX, 2014.

Gathering the input materials took about 3 hours after the simulation was finalized. For another process alternative, all that needs to change is the report files from the process simulator and the stream list which is usually outputted in a designer's normal workflow. There is a database of chemicals so different plants will have a much lower time since the basic chemicals will be automatically outputted with the template. Gathering some of the literature values were done manually for each chemical which can be expedited with the designer's own files or memory since these numbers should be rather common at this stage in the design.

## 6.2 Sanity checks

The methods after *Chem.* were formulated to be theoretically centered on zero. To check this, the average of all parameters and the units were done just for statistical purposes. The result was that the *Secondary Effects*, *Mix*, *Vessel* and *Hotspot* agreed pretty well with this with average values of 0.09, 0.05, 0.02 and 0.04 respectively. *Unit-Unit* is entirely different with a value of 0.54 with the range of numbers between zero to one. This may be an anomaly with the formulation or a function of the case study used.

To understand the output, common knowledge and rules of thumb were checked to see if the index agrees or disagrees. The most definitive trend was in the effect of the unit type with the UDP with the order going compressors, separators, reactors and then heaters. Many dangerous units have a highly mobile solution that is also very toxic mostly due to the presence of carbon monoxide. There is a group of units that have high chemical numbers for fire and expected damage. Some are well managed with the design like with the unit B6 which is near the bottom of the unit list, but some are barely increasing through the other methods which results in a high overall UDP.

*HotSpot* numbers were generally low except for mixers and distillation units. The mixers at the beginning of the plant have large values in Acute toxicity and the Runaway reaction parameters but not Fire or Chronic toxicity. Heaters and reactors have the Fire and Chronic toxicity hazard coming from the evolving chemicals and the general change in temperature throughout the process. This is in line with the namesake of this method coming from temperature monitoring on PFRs.

For the upset conditions, the situation that seemed most influential was a change in flow with changes to pressure more important for utilities and inputs to separators. Thankfully, the safety sensitive units (identified by units that have high *Unit-Unit* streams as inputs) are not the most dangerous units by UDP. This should be expected since the dangerous units may be the ones having the most “dangerous” upsets, sending their “dangerousness” to a unit that may not be able mitigate the hazards. This is highlighted by the units that are most sensitive being those with that are critical for the plant for functioning, like recycle streams, outputs of large separators, and feed streams. This procedure can check if an inherently safer solution is even applicable with the surrounding units or if it degrades the mitigation of hazards in the surrounding units.

The resolution gives rise to design solutions with where redundancy can be helpful and which groups of units may need reworking. Moreover, a designer can see what will be helpful before making detailed calculations. Going back to the equations one can see what changes even affect the system and see if a whole area’s hazards can be reduced. In this case study, when trying to reduce the toxicity of a reactor “2-23” a designer may think that the addition of high level alarms or other monitoring systems would help. However, the real problem here is in chronic toxicity which is above one while acute toxicity is negative. Additionally, all the *Vessel* parameters are negative or zero so efforts should be given to other methods. This means that the best mitigation techniques money can buy will still result in a positive hazard because the minimum value of a *Vessel* parameter is -1. Tracking the numbers back to the chemical components and their compositions, the main contributor of the hazard is from  $H_2$  which is highly mobile, explosive and has a chronic health hazard, which this unit and many other units possess. This has implications on key design variables like the  $H_2:CO$  ratio that governs a lot of hydrocarbon processing facilities. What this procedure can give is a curve between this ratio the economics and the safety portions by tracking different alternatives through the index.

## 7 DISCUSSION

### 7.1 Improvements and the next step

As we seen in the previous section, it is not only the separation between the chemicals, parameters, units and streams that can be examined, trends with unit type and even “spatial” distribution of the units. Communication to different parties can be customized by isolating these factors and telling the story that is relevant for the work relationship. A P&ID design team may be more interested in the stream and spatial orientation, while a chemist might want to improve upon the chemical or unit specific hazards. Related to this is that if you disregard the parameter or method dimensions to the final number, it tells a familiar story throughout the calculations. This allows the numbers to be statistically relevant when being added together and is useful for optimization on the big picture scale. When looking at specific implementations or design decisions, the differences between the parameters and the methods are rich and give insights on how the plant will perform.

To facilitate this exchange of information the output could have sections dedicated to each frame of reference on the problem with the spatial section being an interactive flowsheet with the values imbedded. Just by looking at the unit list one can see units 16-18 and 28, 30 are high which suggests that the overall process in that section is a problem. This is trying to approach a bigger picture mentality than a HazOp review where these units may not be even on the same review section, which would result in separate recommendations for a similar problem.

### 7.2 Conclusions

The IEHS index has been proposed as a tool to support decision making at the conceptual design level. The index quantifies important design decisions with respect to chemical, process equipment, and interactions. The index also addresses the interaction between process design and operability with the additions of failure rates and upset

conditions. The type of information used in the IEHS calculations is appropriate and readily available during process synthesis and preliminary flowsheet screening. The conceptual and physical separation between the different methods and the different parameters used in the index was used extensively to model many different situations and trace back the numbers to the science. The largely independent methods allowed for a statistically relevant aggregation from simple addition. Additionally, it allowed a rudimentary targeting system to be implemented allowing for questions like, “If I focus on this one aspect of the design, what is the largest reduction I can see in the final index value as well as the specific method parameter pair?” A case study has been solved to demonstrate the merits of the proposed index.

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## APPENDIX A

### TABLES

**Table A.1. The phenomenon accounted for when the index is used**

Method	Parameters	Things taken into account / specific model used
Initial Values		
	Mobility	Gas release (MW, $\rho$ ), Flashing liquid, Liquid release (Volatility and Viscosity)
	Fire	Flash point (or predicted) LFL (or predicted) LOC(or predicted)
	Acute Toxicity	TLV-C TLV-STEL IDLH LC <sub>50-inhal</sub>
	Probability of a runaway	Adiabatic temperature rise Auto ignition temperature Self-reactivity
	Expected damage	Reaction Energy Decomposition energy Combustion Energy
	Explosion	Fundamental burning velocity Energy of explosion Maximum Overpressure Oxygen content
	Irritation	LD <sub>50-dermal</sub> SDS info pH
	Chronic Toxicity	TLV-TWA (or predicted)
	Water Effects	Fish (Fathead minnow) LC <sub>50</sub> (or predicted) Small organism (Daphnia magna) LC <sub>50</sub> (or predicted) Bacteria (T. Pyriformis) LC <sub>50</sub> (or predicted)
	Air effects	ERPG2 RfD Chronic toxicity index
	Solid effects	Yes or no (user input)
	Bioaccumulation	Bioaccumulation factor (or predicted)

		Octanol-water partition coefficient (or predicted)
	Degradation	Persistency (or predicted) Half-life (or predicted)
Mixing Factor		
	Mobility	Diffusion interaction (Molar weight, harmonic mean)
	Fire	Presence of the fire triangle LFL <sub>mix</sub> (Heat of combustion) LFL <sub>mix</sub> (Le Chatlier)
	Toxicity	Overall Exposure ToxInfo <sub>mix</sub> (Le Chatlier)
	Probability of a runaway reaction	CRW report
	Explosion	Fundamental burning velocity <sub>mixed</sub> (equivalence ratio) BLEVE
Vessel		
	Failure rate	Literature checked with design specifications
	Extremity of conditions	Literature giving safe operating ranges for a type of vessel
	Alterations	Semi-qualitative user input changing the constants for the previous two examples
Unit-Unit		
	General upset	<ul style="list-style-type: none"> <li>• <i>Vessel</i> average of the upstream model used to determine size of the upset on the current model</li> <li>• Make upset stream for a given variable and guideword (more, less)</li> <li>• 15 min upset of said stream into the current unit (RMP)</li> <li>• If the space time is smaller than 15 minutes, the upset progresses into the next unit until the 15 minutes are up</li> <li>• Redo the index on the entire changed plant</li> <li>• Summation of all the differences between the upset and the normal conditions averaged over all the different types of upsets results in the method value.</li> </ul>